University of Alberta

EVALUATION OF INTRINSIC BIOREMEDIATION OF BTEX AND CHLORINATED HYDROCARBONS AT COLD TEMPERATURES

by

Viola Lai ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Master of Science

in

Geo-Environmental Engineering

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DEDICATION

I would like to thank family, friends, and mentors who have encouraged me throughout the years.

ABSTRACT

The purpose of this investigation is to evaluate the viability of intrinsic bioremediation of BTEX and chlorinated solvents at the former landfill site in CFB Cold Lake, Alberta. Investigations from 1988 to 1998 involved assessments of the soil stratigraphy, the determination of major contaminants that were deposited into the area, the location of the contaminant sources and the delineation of plume extent. The contaminants evaluated include chlorinated aliphatic hydrocarbons (CAHs), such as 1,1,1-trichloroethane (TCA), 1,1-dichloroethane (DCA), and benzene, toluene, ethylbenzene, and xylenes (BTEX). Microcosm tests were set up to represent two sites at two different temperatures (10°C and 20°C), to determine a first order rate of biodegradation. Although no discernable trends were observed in the microcosm tests, the field results indicate that the site conditions are conducive for intrinsic bioremediation. The CAHs and BTEX concentrations are decreasing downgradient from the source, daughter products such as DCA are being formed, and the microbial degradation products such as iron (II) and methane increase in concentration close the source of contamination and downgradient of the source.

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LIST OF ABBREVIATIONS

BTEX	Benzene, Toluene, Ethylbenzene, Xylenes
CAH	Chlorinated Aliphatic Hydrocarbons
1 CEU	1 Construction Engineering Unit
1,2-DCA	1,2-Dichloroethane
DCA	1,1-Dichloroethane
1,2-DCB	1,2-Dichlorobenzene
1,3-DCB	1,3-Dichlorobenzene
1,4-DCB	1,4-Dichlorobenzene
DCE	Dichloroethylene
DO	Dissolved Oxygen
EC	Electrical Conductivity
ETL	Enviro-Test Laboratories
FID	Flame Ionization Detector
GC	Gas Chromatograph
LNAPL	Light Non-Aqueous Phase Liquid
MNA	Monitored Natural Attenuation
PCE	Perchloroethylene
RRMC	Royal Roads Military College
TCA	1,1,1-Trichloroethane
TCE	Trichloroethene
TEAPs	Terminal Electron Accepting Processes
VC	Vinyl Chloride
ΔG	Gibbs Free Energy

1.0 INTRODUCTION

1.1 PROBLEM STATEMENT

An abandoned landfill exists in CFB Cold Lake, Alberta that has been shown to contain harmful contaminants, particularly chlorinated aliphatic hydrocarbons (CAHs), such as 1,1,1-trichloroethane (TCA) and 1,1-dichloroethane (DCA) and benzene, toluene, ethylbenzene, and xylenes (BTEX) (RRMC, 1991). There is a concern that these contaminants may eventually travel from the landfill into Marie Creek, which empties into the Beaver River. Consequently, a study was conducted to:

- identify the nature and extent of the landfill contamination, and
- examine the viability of intrinsic bioremediation for the site.

Dissolved organic contaminants in the groundwater can pose a significant health risk. Hence their reduction to acceptably low concentrations has led to research to evaluate the effectiveness of naturally occurring processes to facilitate their mass removal. Chlorinated aliphatic compounds may occur in older landfills, either intentionally with industrial waste or as trace compounds in other waste types (Kromann et al., 1998). Chlorinated solvents are commonly used for degreasing aircraft engines, automobile parts and electronic components. They are also used in dry-cleaning operations and semiconductor manufacture (Vogel et al., 1987; McCarty and Semprini, 1994). The production and use of halogenated aliphatic compounds in industry and their apparent hazard to human health have prompted investigations concerning their fate in the human body, in subsurface waters, and in treatment facilities (Vogel et al., 1987). Their relatively high solubility and low sorption to soils causes them to migrate downward through soils, and since they are denser than water as free phase, their downward movement is not impeded when they reach the water table, so they can penetrate deeply beneath the water table (McCarty and Semprini, 1994). In particular, TCA is one of four of the most common chlorinated solvents (carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (TCE), and TCA found in contaminated sites and approximately 270 million kg/yr is produced in the United States (Vogel et al., 1987).

BTEX is commonly a result of contamination in groundwater impacted by landfill leachate, coal tar creosote, and petroleum product spills (Barker and Wilson, 1997). BTEX can be released into the ground due to fuel tank spills or leaks, and typically comprises only 2% or 3% (by weight) of the fuel as a whole (Chapelle, 2001). BTEX compounds are highly soluble compared to most of the other hydrocarbons present in gasoline. They are also among the most mobile and most potentially toxic compounds when released to the environment (Chapelle, 2001). It has become evident that microbes can play a major role in the conversion of many of these contaminants to other, usually less harmful, compounds. This natural biological degradation is referred to as intrinsic bioremediation, and it is a key component of monitored natural attenuation (MNA).

1.2 LAYOUT OF THESIS

This thesis evaluates the feasibility of intrinsic bioremediation of CAHs such as TCA and BTEX compounds at an old landfill site in 4 Wing Cold Lake, Alberta. Chapter 2 entails a literature review of the background information on the physical, chemical and biological conditions that are required for the intrinsic bioremediation of CAHs and BTEX. Included in the section are the literature reported rates of degradation and other properties of TCA. Next, Chapter 3 gives a brief site description. Chapter 4 gives an overview of the program of investigation, and includes a discussion of the previous studies done on the site and the field and laboratory methodology. The results are discussed in Chapter 5, after which there is an examination of the implications of the evidence (in Chapter 6) to determine whether the site is conducive to intrinsic bioremediation. Finally, Chapter 7 provides the conclusions and recommendations for future study.

2.0 LITERATURE REVIEW

2.1 DEFINITION OF NATURAL ATTENUATION

Natural attenuation processes include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater (Weidemeier et al., 1998).

Monitored natural attenuation includes the biotic process of intrinsic bioremediation, a series of biochemical reactions mediated by microorganisms that act to break down organic compounds into other substances (Suarez et al., 1999), physical in-situ abiotic processes such as advection, dispersion, and dilution, and chemical processes such as sorption, volatilization, hydrolysis, dehydrohalogenation, hydrogenolysis, and dihaloelimination (Weidemeier et al., 1999).

Intrinsic bioremediation involves the conversion of harmful organic contaminants to less harmful forms through the activity of indigenous microorganisms. In advective transport, solutes are transported by the bulk movement of groundwater. Advection is responsible for the downgradient migration of dissolved contaminants in the subsurface. Dispersion spreads the contaminant plume out laterally, normal to the main direction of groundwater flow, or further downgradient along the main direction of flow, arising largely from the differential rates of movement along individual flow paths through the porous medium (McCarty and Semprini, 1994). Dilution, a dispersion mechanism, results when contaminated groundwater is mixed with clean aquifer water resulting in a reduction in contaminant concentrations and an apparent reduction in the total mass of contaminant in a system (Weidemeier et al., 1995). These three processes do not change the total mass of contaminant that exists in the groundwater; the mass is only transferred to another location. In sorption, contaminants, including chlorinated solvents and BTEX, are removed from solution when the dissolved contaminants partition from the groundwater and adhere to the particles that make up the aquifer matrix. Sorption slows the effective transport velocity of contaminants dissolved in groundwater and because the average velocity of a dissolved contaminant is less than the average seepage velocity of the groundwater, the contaminant is said to be retarded (Weidemeier et al., 1999). In volatilization, contaminants are transformed from dissolved phase in the groundwater into gas phase as soil vapor.

Some abiotic processes that occur for only CAHs are hydrolysis, dehydrohalogenation, hydrogenolysis and dihaloelimination. These processes are discussed in detail in Chapter 2.5.4.

At a particular site, several of the processes mentioned above can occur in conjunction with each other to transform the contaminant plume both physically and chemically. For CAHs, microbial reductive dechlorination and hydrolysis dominate in reducing them to other, sometimes less harmful forms.

2.2 ADVANTAGES AND DISADVANTAGES OF MONITORED NATURAL ATTENUATION

Although monitored natural attenuation has some significant advantages, it also has some limitations. Advantages include:

- smaller volume of remediation wastes reduces potential for cross-media transfer of contaminants and reduced risk of human exposure to contaminated media;
- less intrusion of ground since few surface structures are required;
- potential for application to all or part of the site depending on site conditions and cleanup objectives;
- can be used in conjunction with, or as a follow-up to, other (active) remedial measures; and
- lower overall remediation costs than those associated with active remediation.

Disadvantages include:

- longer time frames to achieve objectives, compared to active remediation;
- site characterization may be more complex and costly;
- toxicity of transformation products may exceed that of the parent compound;
- long-term monitoring will generally be necessary;
- potential exists for continued contamination migration, and/or cross-media transfer of contaminants;
- hydrologic and geochemical conditions amenable to natural attenuation may change over time and could result in renewed mobility of previously stabilized contaminants, adversely impacting remedial effectiveness; and

- more extensive education and outreach efforts may be required in order to gain public acceptance of monitored natural attenuation (Weidemeier et al., 1998).

2.3 GEOCHEMICAL CONDITIONS THAT AFFECT INTRINSIC BIOREMEDIATION

For biodegradation to occur, certain requirements must be met. These requirements include the presence of microorganisms capable of degrading the specific compound, organic carbon or a substrate as an energy and carbon source, electron acceptors, and an adequate supply of nutrients (nitrogen, phosphorus, calcium, magnesium, and iron). Appropriate environmental conditions must also be present, such as temperature, absence of toxic materials, and a pH close to 7 (Lim, 1998). Organic carbon is used as both carbon and energy sources. As a carbon source, the organic carbon is used in conjunction with energy to generate new cells. As an energy source, it is used by the organisms for cell maintenance and growth. The organic carbon is transformed into inorganic carbon, energy and electrons. Approximately 50% of the dry weight of bacteria is carbon (Rifai, 1997).

The microorganisms in groundwater aquifers are usually bacteria and it is preferable to have indigenous microorganisms at a field site which are capable of degrading the contaminants at the site (Rifai, 1997). The microorganisms must have access to the contaminant to be able to metabolize it

Physical and chemical properties of the contaminant that influence its availability include density, water solubility, Henry's constant (H), and the n-octanol/water partition coefficient (K_{ow}). The density of the hydrocarbon free product will affect whether it sinks below the water table or whether it remains above the water table in the vadose zone, where oxygen is available, and anaerobic microorganisms may not be present. If the contaminant is highly soluble and denser than water, it becomes more available to the degrading microorganisms than if the contaminant is less water soluble and less dense than water. The K_{ow} characterizes the hydrophobic nature of the compound and indicates the tendency for the compound to partition or sorb onto soil organic matter. Compounds with low solubility and high K_{ow} tend to sorb strongly to aquifer solids, which retard their movement and decrease their availability for biotransformation. Conversely, contaminants with high water solubility and low K_{ow} are quite mobile and can be transported great distances with ground-water flow. Chlorinated solvents generally have high water solubility and low K_{ow} (Bouwer, 1994). The Henry's constant for chlorinated solvents is also high (> 100 atm) making volatilization an important loss process in open systems, such as the vadose zone or during soil excavation (Bouwer, 1994).

High initial concentrations of organic compounds can be inhibitory to anaerobic microorganisms because the compounds overload and shock the microorganisms. The higher the concentration of organic compounds, the slower the microbial growth rate becomes (Gaudy and Gaudy, 1980). It has been shown for some chlorinated solvents (e.g. DCA, DCE, and TCE in pure methanogenic cultures) that inhibition occurred at exposure concentrations in the range of 50 to 150 mg/L. Partial inhibition (20 to 50% rate decrease) was observed for exposure concentrations in the range of 10 to 50 mg/L (Belay and Daniels, 1987).

2.3.1 Redox Potential Associated with Biodegradation

Oxidation/reduction (redox) potential of groundwater is a measure of electron activity and is an indicator of the relative tendency of a solution to accept or donate electrons. Since redox reactions in groundwater contaminated with hydrocarbons are usually biologically mediated, the redox potential of a groundwater system depends upon and influences rates of biodegradation. Some biological processes operate only within a prescribed range of redox conditions. The redox potential generally ranges from -400 millivolts (mV) (highly reduced) to 800 mV (highly oxidizing). Figure 2-1 shows typical redox conditions for groundwater when different electron acceptors are used.

2.3.2 pH Effects on Biodegradation

The pH of groundwater has an effect on the presence and activity of microbial populations in groundwater. Microbes capable of degrading petroleum hydrocarbon compounds generally prefer pH values varying from 6 to 8 standard units (Weidemeier et al, 1995). TCA transformation by an enrichment culture was observed between pH 6.7 to 8.5 with an optimum between pH 7.4 and 7.6 (de Best et al., 1999). Usually contaminated groundwater has a pH within this range and, thus, no problems are expected for in-situ and on-site biotransformation. However, there may be exceptions like systems that have extremely high or low pH, where the transformation rates may be considerably lower (Wilson et al., 1996).

2.3.3 Electrical Conductivity in Biodegradation

Electrical conductivity is a measure of the ability of a solution to conduct electricity. As the ion concentration in groundwater increases, the conductivity increases. Conductivity measurements are used to ensure that groundwater samples collected at a site are representative of the water in the saturated zone in which the dissolved contamination is present. If conductivities of samples taken from difference sampling points are radically different, the waters may be from different hydrogeologic zones (Weidemeier et al., 1995). For abiotic mechanisms, it has been shown that ionic strength in the ground water and temperature can affect the rate of transformation of chlorinated compounds (Cline and Delfino, 1989). As the ionic strength increases, the abiotic elimination rate increases slightly.

2.3.4 Temperature Effects on Biodegradation

2.3.4.1 Temperature Effects on Microorganisms Behavior

Groundwater temperature affects the metabolic activity of bacteria. Microorganisms have no means of controlling internal temperature; therefore the temperature within the cell is determined by the temperature of the environment (Gaudy and Gaudy, 1980). Biological growth can occur within a wide range of temperatures, but for most organisms the optimum range is 10°C to 35°C. (Wilson et al., 1996). In general, temperatures below the optimum range have a more significant impact on growth rate than temperatures above this range; growth rates approximately double with every 10°C increase until the optimum range is reached (Metcalf and Eddy Inc., 1991; Suarez et al., 1999; Weidemeier et al., 1995). This doubling of hydrocarbon biodegradation rate with

10°C increase is called the Q_{10} rule and applies to a temperature range between 5 and 25°C. Q_{10} is calculated from (Chapra, 1997):

$$Q_{10} = \frac{k(20^{o}C)}{k(10^{o}C)} \qquad [1]$$

Groundwater temperatures less than about 5°C tend to inhibit biodegradation, and slow rates of biodegradation (Weidemeier et al., 1995). de Best et al. (1999) observed TCA to DCA transformation by a methanogenic population at temperatures between 11 °C and 44 °C, with an optimum between 26 °C and 33 °C. No studies were done for temperatures below 11°C because the temperatures in groundwater in the United States were usually between 10°C and 15°C. So it was estimated that the on-site biotransformation of TCA could be significantly reduced with an in-situ temperature less than 10°C. However, de Bruin et al. (1992) found that the dechlorinating microorganisms can adapt to below 15°C without a significant effect on the kinetics of dechlorination.

Although it is generally accepted that biological reaction rates decrease as the temperature decreases, Skeen et al. (1995) reported a laboratory study on the temperature effects on the biodegradation of perchloroethylene, between 17°C and 30°C, which conflicted with this paradigm. They observed that the rate of biodegradation of perchloroethylene was insensitive to temperature, concluding that the dechlorination reaction was not mechanistically different at two temperatures (30°C and 17°C). The reason for the insensitivity was likely to be the existence of cold-adapted microorganisms or abiotic reactions.

2.3.4.2 Temperature Effects on Chemical Equilibrium

Groundwater temperature affects the solubility of oxygen and other geochemical species. Dissolved oxygen is more soluble in cold water than in warm water. Therefore, dissolved oxygen concentraitons in cold temperatures would be expected to be higher than the concentrations in warm temperatures. As well, a change in temperature will affect the chemical properties of organic compounds. Parameters such as solubility, adsorption, and volatilization can change with temperature, with volatilization being most affected, and adsorption the least affected. The effect of temperature on chemical equilibrium can be expressed by the van't Hoff equation, which describes a relationship between the temperature and the equilibrium constant, K (Holman, 1980):

$$\frac{d(\ln k)}{dT} = \frac{\Delta H^{\circ}(T)}{RT^2} \qquad [2]$$

where k is the equilibrium constant, T is the temperature in Kelvin, ΔH^{o} is the enthalpy change, and R is the universal gas constant (8.314 J/mol K). The equilibrium constant in Equation [2] is shown to be directly related to the enthalpy change and the temperature. For reactions in which ΔH^{o} is nearly constant over a range of temperatures, Equation [2] can be integrated between two temperatures, T_1, and T_2 (Holman, 1980):

$$\ln\left(\frac{k_{eq2}}{k_{eq1}}\right) = \frac{\Delta H^{o}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad [3]$$

Thus the equilibrium constant increases with increasing temperature, indicating that more products are formed from the reactants at a higher temperature.

2.3.4.3 Temperature Effects on Chemical Reaction Rates

The influence of temperature on the kinetic rate of a reaction can be expressed using the Arrhenius equation (Reinhard et al., 1997):

$$\ln\left(\frac{k_2}{k_1}\right)=\frac{E_a}{R}\left[\frac{(T_2-T_1)}{T_1T_2}\right] \qquad [4]$$

Where the E_a is the activation energy, R is the universal gas constant, and T is temperature (expressed in Kelvin). This relationship shown in equation [4] shows that as the activation energy increases, the equilibrium constant, k_1, increases.

Since rates measured in ambient temperatures are slow and difficult to measure, rate constants are typically obtained at high temperatures (> 50°C). The Arrhenius equation is then used to extrapolate to ambient temperatures (Reinhard et al., 1997). The activation energies for abiotic transformation of CAHs in aqueous solutions are approximately 100±10 kJ/mol. This translates to a 3.5-fold decrease in reaction rate for each 10°C decrease in temperature, or $Q_{10}=3.5$ (Vogel et al., 1987).

2.4 TERMINAL ELECTRON ACCEPTOR UTILIZATION

Microorganisms and the redox succession are constrained by the laws of thermodynamics (Weidemeier et al., 1995; Kennedy et al., 1999). They can facilitate only those redox reactions that are thermodynamically possible (Chapelle, 1993; Weidemeier et al., 1995). That is, microorganisms will facilitate only those redox reactions that will yield some energy (when $\Delta G^o < 0$). The Gibbs free energy of a reaction at standard state (ΔG^o) is the maximum useful energy change for a chemical reaction at a constant temperature and pressure and is defined by (Weidemeier et al., 1995):

$$\Delta G_r^o = \Sigma \Delta G_{fp}^o - \Sigma \Delta G_{fr}^o \qquad [5]$$

where ΔG_r^o is the Gibbs free energy of a reaction at standard state, $\Sigma \Delta G_{fp}^o$ is the Gibbs free energy of formation of products at standard state, and $\Sigma \Delta G_{fr}^o$ is the Gibbs free energy of formation of reactants at standard state.

The redox potential and the free energy can be related by the Nernst equation (Weidemeier et al., 1998):

$$\Delta G^o = -nFE^o \qquad [6]$$

where E^o is the reductive potential (volts), n is the electron equivalents, and F is Faraday's constant (98487 J/volt-equivalent).

Another form of the equation can give a relationship between temperature, ΔG (free energy), and k_{eq}, the equilibrium constant (Lester and Birkett, 1999):

$$\Delta G^o = -RT \ln K_{eq} \qquad [7]$$

where all terms have been previously defined.

A larger equilibrium constant, K_{eq}, gives a larger Gibbs free energy of the reaction. ΔG increases as more reactants are used up to form products.

Microorganisms will not invest more energy into the system than can be released. A lower energy yielding terminal electron acceptor (TEA) is utilized only if an electron acceptor of a higher energy level has been consumed (Kennedy et al., 1999). Positive ΔG values are indicative of electron donor half-cell reactions and are endothermic. These electron donor reactions include the reactions of BTEX oxidation. Negative ΔG values are indicative of electron acceptor half-cell reactions and are exothermic. These reactions include all of the electron-acceptor reactions. In order to derive energy for cell maintenance and production from BTEX, the microorganisms must couple an endothermic reaction (electron donor oxidation) with an exothermic reaction (electron acceptor reduction). For example, most of the reactions involved in BTEX oxidation cannot proceed abiotically even if thermodynamically favorable, because these reactions require microorganisms to proceed. The microorganisms facilitate these redox reactions by producing enzymes that lower the necessary activation energy for the redox reaction to occur. The requirement of this initial energy input is what prevents these redox reactions from spontaneously occurring in groundwater (Weidemeier et al., 1995). The amount of free energy (ΔG) that can be generated for each of these oxidation/reduction reactions decreases for each successive electron acceptor couple (Kennedy et al., 1999). Figure 2-2 shows a typical change in ΔG values as the process changes from aerobic to anaerobic for BTEX (Weidemeier et al., 1995). As each subsequent electron acceptor is utilized, the groundwater becomes more reducing and the redox potential of the water decreases. The reduction of highly oxidized species results in an overall decrease in the oxidizing potential of the groundwater (Weidemeier et al., 1995).

The order of electron acceptor utilization is shown in Figure 2-3 and is generally:

(Dissolved Oxygen) O_2 > (Nitrate) NO_3^- > (Ferric Iron) Fe^{3+} > (Sulfate) SO_4^{2-} > (Carbon Dioxide) CO_2

Dissolved oxygen is the most favored electron acceptor used in the biodegradation of fuel hydrocarbons because it has the highest energy yield. Upgradient dissolved oxygen concentrations govern the mass of contaminant that can be biodegraded aerobically. Anaerobic bacteria generally cannot function at dissolved oxygen concentrations greater than about 0.5 mg/L (Weidemeier et al., 1995). Microorganisms generally utilize dissolved oxygen and nitrate in areas with dissolved fuel-hydrocarbon contamination at rates that are instantaneous relative to the average advective transport velocity of groundwater. The consumption of these compounds is at a rate approximately equal to the rate at which they are replenished by advective flow processes. Therefore, the use of these compounds as electron acceptors in the biodegradation of dissolved fuel-hydrocarbons is generally accepted to be a mass-transport-limited process (Chapelle, 2001).

After dissolved oxygen has been depleted in the microbiological treatment zone, nitrate may be used as an electron acceptor for anaerobic biodegradation via denitrification. Following the use of nitrate, the oxidizing potential in the groundwater reduces to a level at which iron (III) (ferric iron) reduction can occur. Solid forms of iron in the mineral grains in the form of iron (III) may be used as the electron acceptor. Often, insoluble iron (III) in the form of amorphous iron hydroxides is the most abundant potential electron acceptor (Lovley, 1997). However, only a portion of the total iron present in a given subsurface system is susceptible to direct enzymatic reduction: the biologically available iron (III) fraction. Furthermore, the dissolved form of iron is thought to be more biologically reactive than the solid form (Kennedy et al., 1999). Therefore, iron (III) is reduced to soluble iron (II) (ferrous iron) and the presence of iron (II) in the groundwater is an indicator of iron reduction. When the groundwater is oxygenated the less soluble oxidized from of iron, iron (III), will form and precipitate (Norris, 1994). Ferric iron-reducing organisms can exclude sulfate reduction and methane production from the zone of ferric iron reduction in sediments by out-competing sulfate-reducing and methanogenic food chains for organic matter when ferric iron is available as amorphic ferric oxyhydroxide (Lovley and Philips, 1987).

In some groundwater systems, if the conditions are suitable, manganese (IV) can act as an electron acceptor but is less favorable than iron (III) (Weidemeier et al., 1995).

After dissolved oxygen, nitrate, and bioavailable iron (III) have been depleted in the microbiological treatment zone, dissolved sulfate may be used as an electron acceptor. Because oxygen and nitrate are toxic to sulfate-reducing organisms, if present at high concentrations, sulfate cannot be used as an electron acceptor in the presence of either oxygen or high concentrations of nitrate (Weidemeier et al., 1995). Under sulfate reduction sulfide is produced.

Finally, methanogenesis may occur wherein carbon dioxide is used as an electron acceptor, and methane is produced. Because methane is not present in fuel hydrocarbons or chlorinated solvents, its presence in groundwater above background concentrations in contact with these contaminants is indicative of microbial degradation. Stoichiometry (chemically balanced equations) may be used to estimate the mass of contaminants that may be degraded with the consumption of upgradient oxygen, nitrate, sulfate and the production of downgradient iron (II) and methane. Although electron acceptor utilization is idealized as a series of concentric plumes, the processes may vary on a local scale, depending significantly on the hydrogeologic conditions. Sulfate, iron (III), and carbon dioxide are generally utilized at rates slower than the use of dissolved oxygen and nitrate. This results in consumption of these compounds at a rate that could be slower than the rate at which they are replenished by advective flow processes. Therefore, the use of these compounds as electron acceptors in the biodegradation process may be a reaction-limited process that is approximated by first-order kinetics.

Thus, the dominant terminal electron accepting process can vary both temporally and spatially in an aquifer with fuel hydrocarbon contamination. A given area within an aquifer may switch between iron (III) reduction, sulfate reduction, and methanogenesis depending on seasonal recharge of dissolved oxygen and sulfate recharge and upgradient transport and consumption (Vroblesky and Chapelle, 1994).

2.5 BIOTIC AND ABIOTIC TRANSFORMATION PROCESSES OF ORGANIC COMPOUNDS

The transformation of halogenated aliphatic compounds can be divided into two general classes: reactions that require an external electron transfer (oxidation and reduction) and those that do not (substitution and dehydrohalogenation). External electron transfer is defined as the transfer of electrons to and from some agent other than the halogenated compound itself (Vogel et al., 1987). Table 2-1 shows a list of microorganisms capable of degrading organic compounds under either aerobic or anaerobic conditions (Weidemeier et al., 1995). Under anaerobic conditions, most organic compounds are degraded by a consortium, a group of interacting microorganisms. In the consortium, individual types of organisms carry out different specialized reactions which, when combined, can lead to the complete mineralization of a particular compound (Weidemeier et al., 1998). Figure 2-4 shows the chemical structures of the CAHs and BTEX. Figure 2-5 shows the chemical and microbial degradation pathways of TCA. Figure 2-6 shows the chemical and microbial degradation pathways of benzene and toluene. These pathways will be discussed in detail in the following sections.

2.5.1 Behavior Patterns of CAH Plumes

Chlorinated solvent plumes can degrade in three general patterns depending on the amount of solvent (Type 1); the amount of biologically available organic carbon in the aquifer (Type 2); and the distribution, concentration, and utilization of naturally occurring natural electron acceptors (Type 3) (Weidemeier et al.,1998). Depending on site conditions, a single chlorinated solvent may exhibit different patterns of degradation.

Type 1 behavior occurs when the primary substrate is anthropogenic carbon such as BTEX or landfill leachate, and microbial degradation of this carbon drives reductive dechlorination.

Type 2 behavior is characterized by relatively high concentrations of biologically available native organic carbon and microbial utilization of this carbon drives reductive dechlorination.

Type 3 behavior is exhibited when there is inadequate concentration of native and/or anthropogenic carbon, and concentrations of dissolved oxygen are greater than 1.0 mg/L. This occurs in aerobic environments and reductive dechlorination does not occur.

The more highly chlorinated solvents typically are biodegraded under natural conditions via reductive dechlorination, a process that requires both electron acceptors (the CAHs) and an adequate supply of electron donors.

2.5.2 Mechanisms of Chlorinated Aliphatic Hydrocarbon and BTEX Biodegradation

In biotic transformation, an organic compound can undergo biodegradation as an electron donor, as an electron acceptor, or via cometabolism. Biodegradation can occur in the presence or absence of dissolved oxygen (aerobic or anaerobic conditions). In the first case, the compound serves as a source of carbon and energy (electron donor or substrate), promoting bacterial growth. In the anaerobic respiration process, the compound is used as an electron donor, similar to oxygen in aerobic respiration. In the last case, cometabolism, the subsurface bacteria do not derive any benefits from the degradation, but the compound is biodegraded by an enzyme produced during the degradation of a primary substrate. Depending on the site environmental conditions, one of these processes may dominate or all of these processes may operate concurrently in different portions of the same site (ASCE, 2001). Almost all processes can occur under either aerobic or anaerobic conditions (McCarty and Semprini, 1994).

2.5.2.1 Biodegradation by use of the Organic Compound as the Primary Growth Substrate

BTEX, landfill leachate, natural organic material, chlorobenzenes, and less oxidized chlorinated ethenes and ethanes, can serve as electron donors (Weidemeier et al., 1995). Under aerobic and some anaerobic conditions, the less oxidized chlorinated aliphatic hydrocarbons (eg., VC) can be used as the primary substrate in biologically mediated oxidation-reduction reactions (McCarty and Semprini, 1994). Furthermore, the most common electron acceptors are the TEAs (O_2, NO_3^-, Fe^{3+}, SO_4^{2-}, and CO_2). In this type of reaction, the facilitating microorganisms obtain energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. Microorganisms generally use the least oxidized chlorinated aliphatic hydrocarbons for use as electron donors.

Vinyl Chloride (VC) and 1,2-dichlorethane (1,2-DCA) have been shown to serve as primary substrates under aerobic conditions (McCarty and Semprini, 1994). VC can be mineralized under iron-reducing conditions as long as there is sufficient bioavailable iron (III). 1,1-Dichloroethylene (DCE) ($C_2H_2Cl_2$) has also been shown to mineralize into carbon dioxide under aerobic, iron (III)-reducing, sulfate-reducing, and methanogenic conditions, respectively (Bradley and Chapelle, 1997; Weidemeier et al., 1998). There has been a lack of discussion of aerobic or anaerobic oxidation of chlorinated ethanes (ethanes as the primary substrates) (Weidemeier et al., 1998).

2.5.2.2 Biodegradation by Use of the Organic Compound as an Electron Acceptor

The most important mechanism for biodegradation of TCA and other highly chlorinated solvents such trichloroethene (TCE) or perchloroethylene (PCE) is their use as electron acceptors. This process is referred to as reductive dechlorination, and requires an electron donor (food source). Chlorine atoms are sequentially removed and replaced by hydrogen atoms and the typical electron donors include BTEX compounds and landfill leachate. Figure 2-7 shows TCA transformation to DCA ($Cl_2C_2H_4$) and depicts the loss of the chlorine atom and gain of a hydrogen atom. This sequence might be interrupted if the environment becomes highly oxidized (high concentration of electron acceptors) or if there is a depletion of electron donors (Suarez et al., 1999). Less chlorinated solvents (e.g. DCA) may be degraded either as a substrate aerobically or anaerobically, or utilized as an electron acceptor under highly reduced anaerobic conditions.

Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under sulfate-reducing and methanogenic conditions (Bouwer, 1994). In addition, the extent of dechlorination is highly variable from site to site (Chapelle, 2001). The source of carbon for microbial growth in order for this process to occur is usually natural organic matter, fuel hydrocarbons, or other anthropogenic organic compounds such as those found in landfill leachate. Table 2-2 shows the electron donor and electron acceptor half-cell reactions for reductive dechlorination of TCA and DCA (Weidemeier et al., 1998).

It has been shown that reductive dechlorination is directly related to the availability of molecular hydrogen (Di-Stefano et al., 1991; Concordia et al., 1996; Chapelle, 2001). Therefore, the efficiency of reductive dechlorination is directly related to the availability of H_2, which is controlled by ambient microbial terminal electron-accepting-processes (TEAPs). H_2 is continuously produced by fermentative microorganisms metabolizing natural or anthropogenic organic matter. This H_2 is then utilized by respirative microorganisms that most commonly use Fe(III), sulfate, or CO_2 as terminal electron acceptors. Significantly, each of these TEAPs has a different affinity for H_2 uptake (Lovley and Goodwin, 1988). CO_2 reduction (methanogenesis) has the lowest H_2 affinity, and causes the H_2 concentrations in groundwater to be relatively high. Sulfate reduction, Fe (III) reduction, and nitrate reduction have progressively greater affinities for H_2 and are characterized by progressively lower steady-state H_2 concentrations. Consequently, the observation that reductive dechlorination is more efficient under methanogenic or sulfate-reducing conditions is due to the greater availability of H_2 (Chapelle, 2001).

If the environment is depleted of electron donors before the chlorinated aliphatic hydrocarbons are degraded, biological reductive dechlorination will cease, and natural attenuation may no longer be protective of human health and the environment. This difference between the process of fuel hydrocarbon and CAH biodegradation makes it more difficult to predict the long-term behavior of CAH plumes (Weidemeier et al., 1998).

2.5.2.3 Cometabolism

In cometabolism, which is best documented in aerobic environments, but can also occur under anaerobic conditions, an enzyme or cofactor that is produced by the organisms for other purposes, catalyzes the degradation. The organisms receive no known benefit from the degradation of the chlorinated aliphatic hydrocarbon, and the degradation may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994). CAHs such as TCE, DCE and VC have been reported to undergo cometabolism (Chapelle, 2001).

2.5.3 Biodegradability of BTEX

Under ideal conditions, the biodegradation rates of the low to moderate weight aliphatic, alicyclic, and aromatic compounds can be very high. As the molecular weight of the compound increases, so does the resistance to biodegradation (Malone et al., 1993). In most subsurface environments, aerobic biodegradation can occur in addition to anaerobic biodegradation near the margins of the plume where dispersion helps spread the plume into more highly oxygenated regions of the aquifer (Weidemeier et al., 1995).

The biodegradation of fuel hydrocarbons, especially BTEX, is mainly limited by electron acceptor availability, and generally will proceed until all of the contaminants biochemically accessible to the microbes are destroyed. Weidemeier et al. (1998), claim that there appears to be an adequate supply of electron acceptors in most, if not all, hydrogeologic environments.

Anaerobic fermentation of BTEX is likely to occur under all anaerobic conditions (Chapelle, 2001). It appears that toluene, ethylbenzene, and the xylenes are degradable under denitrifying conditions in groundwater, but benzene degradation under denitrifying conditions is questionable since it appears that only one field example shows its slow biotransformation (Barker and Wilson, 1997). Several field studies have shown the anaerobic biodegradation of monoaromatic hydrocarbons in denitrification (Barbaro et al., 1992; Hutchins and Wilson, 1991; Barker et al, 1997), iron/manganese reduction (Lovley and Lonergan, 1990; Lyngkilde and Christensen, 1992), sulfate-reduction (Acton and Barker, 1992; Beller et al., 1992; Thierrin et al., 1992; Edwards et al., 1991), and methanogenesis (Wilson et al., 1992; Reinhard et al., 1984; Barker et al., 1987; Barker and Wilson, 1997). In anaerobic conditions, benzene may degrade by ring oxidation, forming phenol, or reduction, forming cyclohexene (Figure 2-6). The degradation proceeds through a number of oxidation steps to form carboxylic acids, which are then further oxidized to CO_2 and CH_4. Toluene may undergo ring oxidation to form p-cresol or o-cresol. Reduction of the toluene ring can also occur, producing methylcyclohexane. If its methyl group is oxidized with the formation of benzyl alcohol, it can be further oxidized to benzoate and then to carboxylic acids (Chapelle, 2001).

2.5.4 Abiotic CAH Degradation

Bioremediation is considered as a useful tool only if complete dechlorination can be achieved. Because of the influence of biological activity on chemical conditions and vice versa, it can be difficult to attribute CAH disappearance to solely either chemical or biological factors. Biological and chemical transformations may also occur sequentially and competitively. Biotic transformations of chlorinated solvents under anaerobic conditions generally occur in conjunction with abiotic process such as either hydrogenolysis or dihaloeliminaton (McCarty and Semprini, 1994).

Hydrolysis and dehydrohalogenation are the most thoroughly studied abiotic attenuation mechanisms for chlorinated solvents. In hydrolysis, the compound reacts with water, and a halogen substituent is replaced with a hydroxyl (OH^-) group. Hydrolysis results in reaction products that may be more susceptible to biodegradation, as well as more soluble. Dehydrohalogenation is an elimination reaction involving halogenated alkanes in which a halogen is removed from one carbon atom, followed by subsequent removal of a hydrogen atom from an adjacent carbon atom. In this two step reaction, an alkene is produced. Contrary to the patterns observed for hydrolysis, the likelihood that dehydrohalogenation will occur increases with the number of halogen substituents (Vogel et al., 1987; Weidemeier et al., 1999). Two reductive dechlorination reactions that may operate in the subsurface are hydrogenolysis and dihaloelimination. The first is the simple replacement of a chlorine (or another halogen) by a hydrogen, while dihaloelimination is the removal of two chlorines (or other halogens) accompanied by the formation of a double carbon-carbon bond (Weidemeier et al., 1999).

Although the formal oxidation state of a halogenated aliphatic compound decreases as a result of the loss of a halogen, it increases with the loss of hydrogen. Thus, dehydrohalogenation reactions do not include external electron transfer, and no net change occurs in the oxidation state of the reacting molecule (Vogel et al., 1987).

2.5.5 Microbial Transformation of TCA

TCA is a highly volatile organic compound and degrades under mostly methanogenic conditions (Kromann et al., 1998). TCA may be transformed by anaerobic microbial mineralization or reductive dehalogenation to form DCA and chloroethane (ClC_2H_5, CA) (de Best et al., 1999; Reinhard et al., 1997; Vogel and McCarty; 1987). The microbial degradation of TCA into its daughter compounds, DCA and CA is illustrated in Figure 2-7. DCA and CA can generally be degraded under aerobic conditions.

However, since the transformation of DCA under anaerobic conditions is much slower than CA transformation, it is preferable to have the complete transformation of TCA to CA either without the formation of DCA or without leaving residual DCA (de Best et al., 1999). DCA and chloroethane can then be hydrolyzed to ethanol, which can be rapidly mineralized by microorganisms (Vogel et al., 1987), or dehydrohalogenated to vinyl chloride (chloroethene, C_2H_3Cl, VC) (Jeffers et al., 1989; Smith and Dragun, 1984; Weidemeier et al., 1999). Other studies indicate that the microbial degradation of TCA can yield *cis*-1,2-DCE, *trans*-1,2-DCE, as well as DCA and CA (Bouwer and McCarty, 1983; Parsons et al., 1985).

2.5.6 Abiotic Transformation of TCA

In the absence of microbial degradation, TCA can be transformed directly by abiotic processes such as hydrolysis and dehydrohalogenation. McCarty (1996) lists 1,1,1-TCA as the only major chlorinated solvent that can be transformed chemically through hydrolysis and elimination (dehydrohalogenation). Reductive reactions (including hydrolysis and dehydrohalogenation) are commonly microbially mediated (Butler and Parker, 1996). By hydrolysis, TCA is transformed to hydrochloric acid and acetic acid (a major product) but by elimination, TCA also transforms into DCE (a minor product) (Reinhard et al., 1997; Vogel and McCarty; 1987; McCarty, 1996; Gerkens and Franklin, 1989). Acetic acid, the product of hydrolysis is chemically inert, but it can be mineralized rapidly by microorganisms. The product of dehydrohalogenation, DCE, can then be transformed further by reductive dehalogenation to VC under methanogenic conditions (Weidemeier et al., 1999). The VC is then either reductively dehalogenated to ethene or consumed as a substrate in an aerobic reaction and converted to carbon dioxide (Weidemeier et al., 1999).

The decreasing reductive potential, coupled with the decreasing number of chlorine atoms often causes abiotic degradation of TCA to be incomplete and leads to the accumulation of cis-DCE and VC in ground water. Since DCE is more toxic than TCA, the conversion to DCE in groundwater can increase the toxicity of the water supply (Cline and Delfino, 1989).

2.5.7 Further Transformation of TCA Daughter Products

Sequential anaerobic/aerobic transformations of CAHs often occurs, in which the TCA is transformed to a less chlorinated compound via anaerobic degradation and the less chlorinated daughter products are further degraded by aerobic microorganisms. This oxidative process often results in complete mineralization to carbon dioxide. It is mediated by three general mechanisms: incorporation of oxygen in the carbon-hydrogen bond, oxidation of a halogen substituent, and oxidation of a carbon-carbon double bond via epoxidation (Bouwer, 1994).

Figure 2-8 shows the relationships between degree of chlorination and anaerobic reductive dechlorination, aerobic degradation and sorption onto subsurface material. It has been observed that more chlorinated compounds are more easily reductively dechlorinated than less chlorinated compounds (Fathepure et al., 1987). The reductive dechlorination of VC, the least oxidized of the chloroethenes, to ethene is often slow and is significant only under highly reducing, methanogenic conditions (Chapelle, 2001; Freedman & Gossett, 1989; Di-Stefano et al., 1991; Bouwer, 1994). Furthermore, it appears that sorption onto subsurface material increases with the degree of chlorination (Vogel, 1994).

The efficiency of aerobic degradation increases for less chlorinated compounds (Davis & Carpenter, 1990; Phelps et al., 1991). As the least chlorinated of the chloroethenes, VC has the greatest tendency to undergo oxidation. Rapid microbial degradation of VC, including mineralization, has been observed in laboratory cultures and aquifer samples under aerobic conditions (Chapelle, 2001; Davis and Carpenter, 1990; Phelps et al., 1991; Bradley and Chapelle, 1996). Davis and Carpenter (1990) conducted studies to examine the biodegradation of vinyl chloride in samples taken from a shallow aquifer. Under aerobic conditions, VC was readily degraded, with greater than 99% of the labeled material being degraded after 108 days and approximately 65% being mineralized to CO_2. Moreover, under aerobic conditions, VC can be used as a sole carbon source for growth and metabolisms (Chapelle, 2001; Hartmans et al., 1985; Hartmans and de Bont, 1992). DCE, on the other hand, has been shown to oxidize under aerobic conditions in liquid culture, but this oxidation apparently does not support microbial growth (Chapelle, 2001). The oxidation reactions that transform VC and DCE are shown below:

VC

$ClC_2H_3 + 5/2O_2 \text{->} 2CO_2 + H_2O + H^+ + Cl^-$

DCE

$Cl_2C_2H_2 + 2O_2 \text{->} 2CO_2 + 2H^+ + 2Cl^-$

Because the production of DCE and VC generally occur by reductive dechlorination under anaerobic conditions, the aerobic oxidation of these compounds is often limited in ground-water systems. However, where anaerobic conditions that produce DCE and VC grade to more oxic conditions, which often happens on the fringes of contaminant plumes, aerobic oxidation of these compounds can be significant (Chapelle, 2001).

2.5.8 Distribution of Biotic and Abiotic Transformation Products of TCA

It is estimated that, due to abiotic processes alone, approximately 20% of the TCA is converted to DCE, while 80% is transformed into acetic acid (Weidemeier et al., 1999; McCarty, 1996; Haag & Mill, 1988; Dilling et al., 1975; Gerkens And Franklin, 1989; Vogel and McCarty, 1987). The ratio for the rates of hydrolysis to elimination is approximately 3:1. Figures 2-9 and 2-10 show estimated distributions of TCA transformation products (Vogel, 1994). Figure 2-9 shows the approximate percent of distribution of degradation products for chemical degradation alone. TCA is assumed to be almost completely degraded into its chemical degradation products, and acetic acid and DCE make up 80% and 20% of the total degradation products, respectively. Figure 2-10 shows the distribution of microbial and chemical degradation products for low microbial activity and high microbial activity. Under lower microbial activity, after 20 years, more acetic acid is formed than the rest of the products. However, with higher microbial activity, the microbial product, DCA makes up the majority of the products, approximately 65% of the total, while DCE and acetic acid make up approximately 3 to 5%. Butler and Barker (1996) note that attributing changes in the concentration of chlorinated solvents to abiotic processes is usually difficult. For example, microbial activity is generally required to produce the reducing conditions for reductive dehalogenation. Furthermore, to determine that hydrolysis is occurring, the presence of acetic acid must be observed but these products are usually more easily biodegraded than their parent compounds and can be difficult to detect (Butler and Barker, 1996). If biodegradation is occurring at a site, the loss of contaminant mass due to that process may dwarf the mass lost to abiotic reactions. Rates of abiotic degradation may be slow relative to biotic mechanisms, but the contribution of these mechanisms may still play a significant role in natural attenuation, depending on the site conditions (Weidemeier et al., 1998). Some of the by-products of chlorinated compounds may be more easily or less easily degraded than the parent compound; therefore the contributions of abiotic mechanisms may be important and needs to be considered when evaluating a site.

2.6 LITERATURE REPORTED REACTION RATES FOR DEGRADATION OF TCA, DCA, AND BTEX

First order kinetics are often used to model the rate of transformation of the "parent" compound into breakdown products. The general equation for first-order decay is:

$$C_t = C_0 e^{-kt} \qquad [8]$$

where C_t = contaminant concentration at time t

C_0 = initial contaminant concentration

k = first-order decay constant (total attenuation rate)

t = time

This equation is used for determining apparent first order rates for TCA degradation.

Table 2-3 shows some reported first order degradation reaction rates for TCA.

The rate of utilization of primary substrate for bacterial growth is often represented by the Monod relationship:

$$\frac{-d[S]}{dt}=\frac{k[X][S]}{[S]+K_s} \qquad [9]$$

where [S] is the concentration of the primary substrate, [X] is the concentration of active biomass, k is the maximum rate coefficient of substrate utilization, and K_s is the half-velocity coefficient (Galli and McCarty, 1989). Another format for the equation is:

$$\frac{-d[S]}{dt}=Y_{sx}\mu_{max}\frac{k[X][S]}{[S]+K_s} \qquad [10]$$

where [X] represents the aqueous biomass concentration (mg-DW/L); [S] the substrate concentration (mol/L); μ_{max} is the maximum growth rate (day^{-1}) (Skeen et al., 1995). Equations [7] and [8] are sometimes used to determine rates of degradation for compounds such as BTEX in situations where BTEX is used as the substrate.

Degradation of TCA is generally expected to be dominated by microbial degradation. Rates of microbial reductive dehalogenation vary widely with environmental conditions, but are potentially greater than for abiotic processes (Wing, 1997; Vogel and McCarty, 1987; Vogel et al., 1987).

There are more abiotic degradation rates reported in literature than rates for biodegradation, possibly due to the difficulty in determining biotic transformation rates.

In summary, the biotic transformation half lives reported range from 0.38 to 1.5 years, the abiotic transformation half lives range from 0.5 to 19 years, and the total transformation half life (one reported) is approximately 2.3 years.

2.7 LINES OF EVIDENCE FOR INTRINSIC BIOREMEDIATION

According to Weidemeier et al. (1999), several criteria are used to evaluate a site to determine its suitability for natural attenuation. These include:

- Historical trends in contaminant data showing plume stabilization and/or loss of contaminant mass over time. Nondestructive mechanisms of natural attenuation such as dilution, dispersion, sorption, and volatilization may be sufficient to cause the dissolved contaminant plume to reach steady-state.
- Analytical data showing that geochemical conditions are suitable for biodegradation and that active biodegradation has occurred, such as:
  a) depletion of electron acceptors and donors;
  b) increasing metabolic by-product concentrations;
  c) decreasing parent compound concentrations;
  d) increasing daughter compound concentrations;
- microbiological data that support the occurrence of biodegradation

Weidemeier et al. (1998) also identified a fourth line of evidence to be used to estimate natural attenuation which was to obtain data from the field or microcosm studies to demonstrate the occurrence of biological degradation at the site and its ability to degrade the contaminants of concern.

Weidemeier et al. (1999) have developed a preliminary scoring system for evaluating the potential for anaerobic biodegradation of CAHs. Their system assigns points for qualities of the site that represent optimal conditions for bioremediation. It is designed to recognize the geochemical environments in which reductive dechlorination is plausible. The closer a site is to optimum, the more points are assigned to that site. It is intended for chlorinated solvents for which the initial biotransformation in the environment is reductive dechlorination. For less halogenated compounds such as dichloroethane, chloroethane, or vinyl chloride, which can be biodegraded aerobically, this scoring system is only applicable to the anaerobic portion of their degradation (Weidemeier et al., 1999). Table 2-4 and Table 2-5 show the Weidemeier et al. (1995) scoring system. The scoring system was applied to the landfill site. The results are shown in section 5.2.2.

Table 2-1: Microorganisms Capable of Degrading Organic Compounds (Modified From Weidemeier et al., 1995)

Contaminant	**Microorganisms**	**Comments/Biodegradability**
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa, Acintobacter sp., Methylosinus trichlosporium* OB3b, *Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichlosporium* OB3b, *Bacillus sp., Pseudomonas sp., P. putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, P. aeruginosa, Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylenes	*Pseudomonas putida, methanogens, anaerobes*	High
Jet Fuels	*Cladosporium, Hormodendrum*	High
Kerosene	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Canadidaparapsilosis, C. guillermondii, C. lipolytica, Trichlosproron sp., Rhohosporidium toruloides, Cladosporium resinae*	High
Chlorinated Ethenes	*Dehalobacter restrictus, Dehalospirillum multivorans, Enterobacter agglomerans, Dehalococcus entheogenes strain* 195, *Desulfitobacterium sp. Strain* PCE1, *Pseudomonas putida* (multiple strains), *P. cepacia* G4, *P. mendocina, Desulfobacterium sp., Methanobacterium sp., Methanosarcina sp. Strain DCM, Alcaligenes eutrophus* JMP 134, *Methylosinus trichlosporium* OB3b, *Escherichia coli, Nitorsomonas europaea, Methylocystis parvus* OBBP, *Mycobacterium sp., Rhodococcus erythopolis*	Moderate
Chlorinated Ethanes	*Desulfobacterium sp., Methanobacterium sp., Pseudomonas putida, Clostridium sp., C. sp. Strain* TCAIIB	Moderate
Chlorinated Methanes	*Acetobacterium woodii, Desulfobacterium sp., Methanobacterium sp., Pseudomonas sp. Strain* KC, *Escherichia coli* K-12, *Clostridium sp., Methanososarcina sp., Hyphomicrobium sp. Strain* DM2	Moderate
Chlorobenzenes	*Alcaligenes sp.* (multiple strains), *Pseudomonas sp.* (multiple strains), *P. putida, Staphylococcus epidermis*	Moderate to High

Table 2-2: Electron Donor and Electron Acceptor Half-Cell Reactions (Modified From Weidemeier et al., 1998)

Half-Cell Reactions	ΔG°_{r}(kcal/equiv)	ΔG°_{r}(kJ/equiv)	E°(V)	Eh (V)	pe
ELECTRON-ACCEPTOR (REDUCTION) HALF-CELL REACTIONS					
$3e^- + 6H^- + NO_3^- \gamma\ 0.5N_2 + 3H_2O$ Denitrification	-28.7	-120.0	+1.24	+0.708	+12.0
$4e^- + 4H^+ + O_2 \gamma\ 2H_2O$ Aerobic Respiration	-28.3	-119.0	+1.23	+0.805	+13.6
$8e^- + 10H^- + NO_3^- \gamma\ NH_4^- + 3H_2O$ Nitrate Reduction	-20.3	-84.9	+0.879	+0.362	+6.12
$2e^- + 2H^+ + NO_3^- \gamma\ NO_2^- + H_2O$ Nitrate Reduction	-18.9	-78.9	+0.819	+0.404	+5.32
$8e^- + 9H^+ + SO_4^{2-} \gamma\ HS^- + 4H_2O$ Sulfate Reduction	-5.74	-24.0	+0.249	-0.278	-4.70
$8e^- + 10H^+ + SO_4^{2-} \gamma\ H_2S^0 + 4H_2O$ Sulfate Reduction	-6.93	-28.9	+0.301	-0.143	-2.42
$8e^- + 8H^- + CO_{2(g)} \gamma\ CH_{4(g)} + 2H_2O$ Methanogenesis	-3.91	-16.4	+0.169	-0.259	-4.39
$C_2H_3Cl + H^+ + 2e^- \gamma\ C_2H_4 + Cl^-$ VC Reductive Dechlorination	-13.75	-57.5	+0.596	+0.507	+8.57
$C_2H_2Cl_4 + H^+ + 2e^- \gamma\ C_2H_3Cl_3 + Cl^-$ PCA Reductive Dechlorination	-13.59	-56.8	+0.589	+0.500	+8.45
$C_2H_3Cl_3 + H^+ + 2e^- \gamma\ C_2H_4Cl_2 + Cl^-$ TCA Reductive Dechlorination	-15.26	-63.8	+0.661	+0.572	+9.67
$C_2H_4Cl_2 + H^+ + 2e^- \gamma\ C_2H_3Cl + Cl^-$ DCA Reductive Dechlorination	-14.08	-58.9	+0.610	+0.321	+8.81

Table 2-2: (Cont'd)

Half-Cell Reactions	ΔG°_r(kcal/equiv)	ΔG°_r(kJ/equiv)	E°(V)	Eh (V)	pe
ELECTRON-ACCEPTOR (REDUCTION) HALF-CELL REACTIONS					
$12H_2O + C_6H_6 \; \gamma \; 6CO_2 + 30H^+ + 30e^-$ Benzene Oxidation	+2.83	+11.8	-0.122	+0.316	+5.34
$14H_2O + C_6H_5CH_3 \; \gamma \; 7CO_2 + 36H^+ + 36e^-$ Toluene Oxidation	+2.96	+12.4	-0.128	+0.309	+5.22
$16H_2O + C_6H_5C_2H_5 \; \gamma \; 8CO_2 + 42H^+ + 42e^-$ Ethylbenzene Oxidation	+2.96	+12.4	-0.128	+0.309	+5.21
$4H_2O + C_2H_2Cl_2 \; \gamma \; 3CO_2 + 10H^+ + 8e^- + 2Cl^-$ DCE Oxidation	-3.88	-16.2	+0.168	-0.131	-2.21
$4H_2O + C_2H_3Cl \; \gamma \; 2CO_3 + 11H^+ + 10e^- + Cl^-$ Vinyl Chloride Oxidation	-0.55	-2.3	+0.024	-0.006	-0.10
$2H_2O + C_6H_4Cl_2 \; \gamma \; 6CO_2 + 28H^+ + 26e^- + 2C$ Dichlorobenzene Oxidation	+1.40	+5.84	-0.060	-0.071	-1.21
$12H_2O + C_6H_5Cl \; \gamma \; 6CO_2 + 29H^+ + 28e^- + Cl^-$ Chlorobenzene Oxidation	+2.22	+9.26	-0.096	-0.0107	-1.80

NOTES:

ΔG°_r for half-cell reaction as shown divided by the number of electrons involved in reaction.

E° calculated using the following equation: $E^\circ = \Delta G^\circ_r(J/nF) * 1.0365\times10^{-3}$ (VF/J) from Stumm and Morgan, 1981.

Table 2-3: Literature Reported First Order Transformation Rates for TCA

Half-life (yrs)	Temperature (°C)	Reference	Process
1.5 to 3	?	Howard et al., 1991	Anaerobic biodegradation
0.38 to 1.5	?	Howard et al., 1991	Aerobic biodegradation
0.044	?	Wood et al., 1981, 1985	Anaerobic biodegradation
0.12 to 0.56	20	Klecka et al., 1990	Anaerobic biodegradation
<0.003		Vogel and McCarty, 1987	Anaerobic biodegradation
2.3	15	Wing, M. 1997	Total degradation (both biotic and abiotic)
<0.005		Bouwer and McCarty, 1983	Microbial degradation
2.9	15	Wing, M. 1997	Hydrolysis
0.95	20	McCarty, 1996	Hydrolysis
12	10	McCarty, 1996	Hydrolysis
0.5	25	Dilling et al., 1975	Hydrolysis
0.9	25	Ellenrieder et al., 1988	Hydrolysis
2.2	20	Ellenrieder et al., 1988	Hydrolysis
0.96	25	Haag and Mill., 1988	Hydrolysis
1.1	25	Jeffers et al., 1989	Hydrolysis
1.7	20	Gerkens and Franklin, 1989	Hydrolysis
2.8 and 19	20	Vogel and McCarty, 1987	Hydrolysis
3.16 to 3.81	20	Klecka et al., 1990	Hydrolysis
1.59	?	Semprini et al., 1992	Hydrolysis
2	15	McNab et al., 1994	Hydrolysis
0.81		Cline and Delfino., 1989	Hydrolysis
1.7	20	Mabey et al., 1983	Hydrolysis to Acetic Acid
0.8	10	Pearson and McConnell, 1975	Hydrolysis to DCE
0.83	25	Washington, 1995	Hydrolysis
10.3	10	Washington, 1995	Hydrolysis
0.81	35	Galli and McCarty, 1989	Hydrolysis to DCE

Table 2-4: Weidemeier et al., 1999 Scoring System (Modified From Weidemeier et al., 1999)

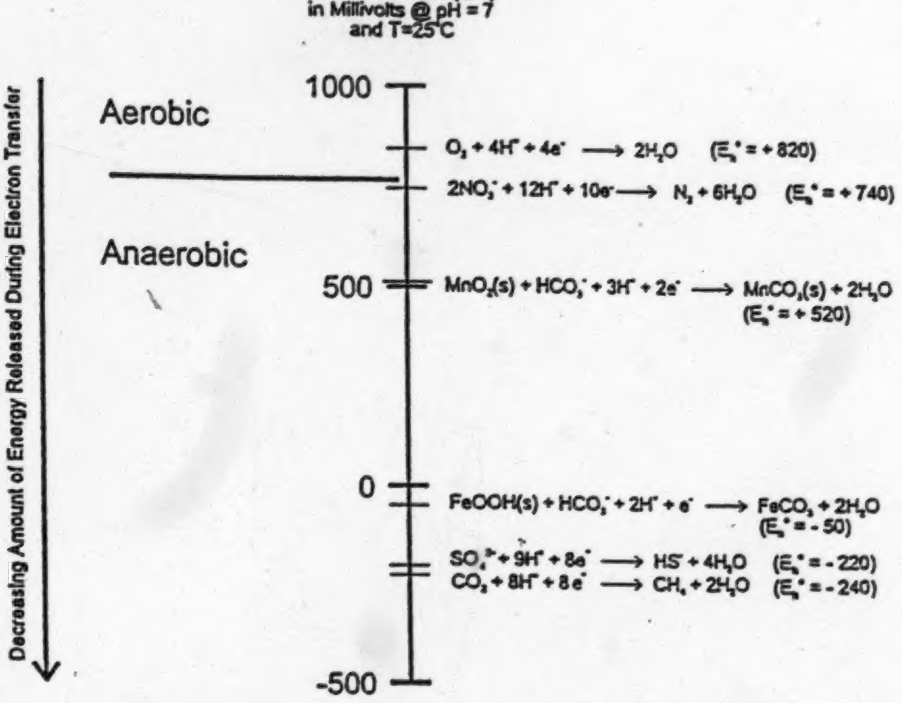
Analysis	Concentration in Most Contaminated Zone	Interpretation	Value
Oxygen	< 0.5 mg/L	Tolerated, suppresses reductive pathway at higher concentrations	3
Oxygen	> 1 mg/L	VC may be oxidized aerobically	-3
Nitrate	< 1 mg/L	May compete with reductive pathway at higher concentrations	2
Fe(II)	> 1 mg/L	Reductive pathway possible: VC may be oxidized under Fe (III)-reducing conditions	3
Sulfate	< 20 mg/L	At higher concnetrations may compete with reductive pathway	2
Methane	< 0.5 mg/L	VC oxidizes	
	> 0.5 mg/L	Ultimate reductive daughter product; VC accumulates	0 3
Oxidation reduction potential (ORP)	< 50 mV	Reductive pathway possible	1
	< -100 mV	Reductive pathway likely	2
pH	5 < pH < 9	Optimal range for reductive pathway	0
	5 > pH > 9	Outside optimal range for reductive pathway	-2
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2
Temperature	> 20°C	At T>20°C, biochemical process is accelerated	1
Carbon dioxide	> 2 x background	Ultimate oxidative daughter product	1
Alkalinity	> 2 x background	Results from interaction of carbon dioxide with aquifer minerals	1
Chloride	> 2 x background	Daughter product of organic chlorine	2
Hydrogen	> 1 nM	Reductive pathway possible: VC may accumulate	3
Hydrogen	< 1 nM	VC oxidized	0
Volatile fatty acides	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	2
BTEX	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2
Tetrachloroethene	--	Material released	0
		Daughter product of PCE	2[1]
Trichlorethene	--	Material released	0
DCE	--	Material released	0
		Daughter product of TCE (If cis is greater than 80% of total DCE, it is probably a daughter product of TCE 1,1-DCE can be chemical reaction product of TCA)	2[1]
VC	--	Material released	0
		Daughter product of DCE	2[1]
1,1,1-Trichloroethane	--	Material released	0
DCA	--	Daughter product of DCA or VC under reducing conditions	2
Carbon tetrachloride	--	Material released	0
Chloroethane	--	Daughter product of DCA or VC under reducing conditions	2
Ethene/ethane	> 0.01 mg/L	Daughter product of VC/ethene	2
	> 0.1 mg/L		3
Chloroform	--	Material released	0
		Daughter product of carbon tetrachloride	2
Dichloromethane	--	Material released	0
		Daughter product of chloroform	2

[1] Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

Table 2-5: Interpretation of Weidemeier et al., 1999 Scoring System (Weidemeier et al., 1999)

Score	Interpretation
0-5	Inadequate evidence for anaerobic degradation[1] of chlorinated organics
6-14	Limited evidence for anaerobic degradation[1] of chlorinated organics
15-20	Adequate evidence for anaerobic biodegradation[1] of chlorinated organics
> 20	Strong evidence for anaerobic biodegradation[1] of chlorinated organics

[1] Reductive Dechlorination



Redox Potential (Eh°) in Millivolts @ pH = 7 and T=25°C
Decreasing Amount of Energy Released During Electron Transfer
Aerobic
Anaerobic
1000
500
0
-500
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ ($E_w^\circ = +820$)
$2NO_3^- + 12H^+ + 10e^- \longrightarrow N_2 + 6H_2O$ ($E_w^\circ = +740$)
$MnO_2(s) + HCO_3^- + 3H^+ + 2e^- \longrightarrow MnCO_3(s) + 2H_2O$ ($E_w^\circ = +520$)
$FeOOH(s) + HCO_3^- + 2H^+ + e^- \longrightarrow FeCO_3 + 2H_2O$ ($E_w^\circ = -50$)
$SO_4^{2-} + 9H^+ + 8e^- \longrightarrow HS^- + 4H_2O$ ($E_w^\circ = -220$)
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$ ($E_w^\circ = -240$)

Figure 2-1: Redox Potential versus Electron Donors and Acceptors in the Biotransformation Process (Modified from Weidemeier et al., 1998)

Process	ΔG
Aerobic Respiration	-3202
Denitrification	-3245
Sulfate Reduction	-2343
Iron (III) Reduction	-514
Methanogenesis	-136

Figure 2-2: Typical Change in Gibbs Free energy, ΔG Values with Change in Electron Accepting Process (Modified From Weidemeier et al., 1995)

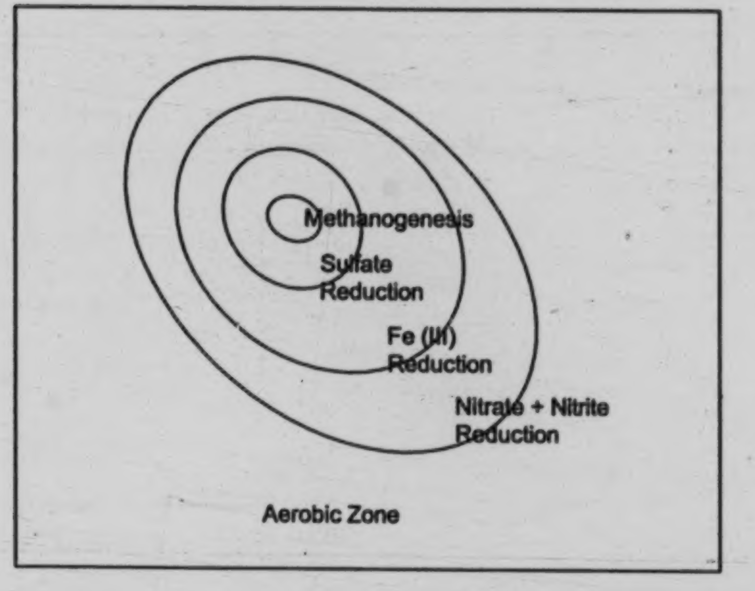

Methanogenesis
Sulfate Reduction
Fe (III) Reduction
Nitrate + Nitrite Reduction
Aerobic Zone

Figure 2-3: General Electron Acceptor Utilization (Modified From Bouwer, 1994)

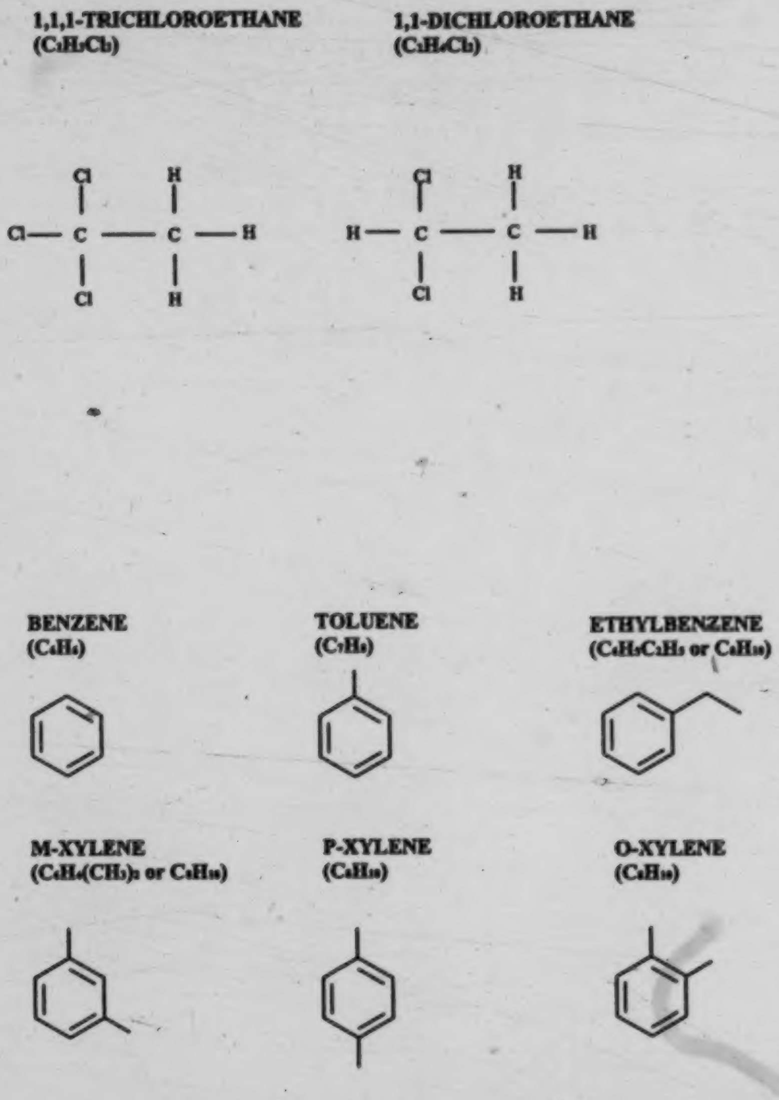

1,1,1-TRICHLOROETHANE
($C_2H_3Cl_3$)
1,1-DICHLOROETHANE
($C_2H_4Cl_2$)
BENZENE
(C_6H_6)
TOLUENE
(C_7H_8)
ETHYLBENZENE
($C_6H_5C_2H_5$ or C_8H_{10})
M-XYLENE
($C_6H_4(CH_3)_2$ or C_8H_{10})
P-XYLENE
(C_8H_{10})
O-XYLENE
(C_8H_{10})

Figure 2-4: Chemical Structures of BTEX and Chlorinated Aliphatic Hydrocarbons (Modified From Verschueren, 2000)

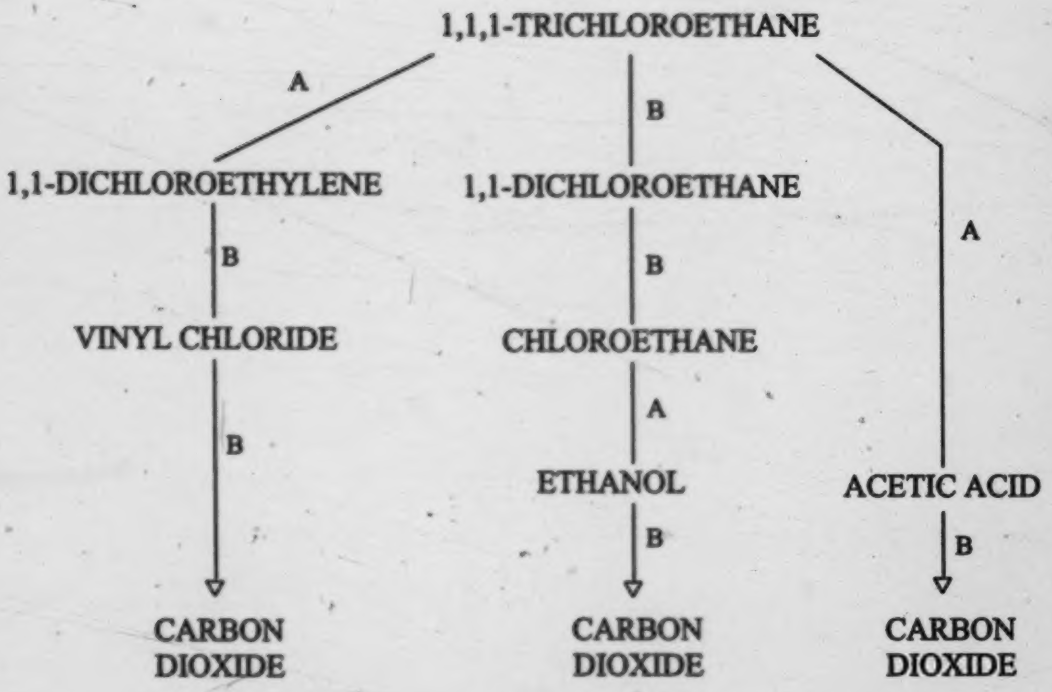
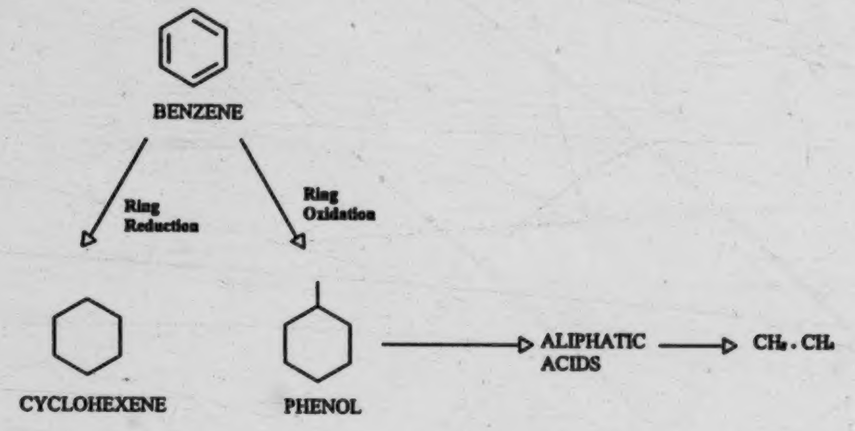

1,1,1-TRICHLOROETHANE
A
B
1,1-DICHLOROETHYLENE
1,1-DICHLOROETHANE
A
B
B
VINYL CHLORIDE
CHLOROETHANE
A
B
ETHANOL
ACETIC ACID
B
B
CARBON DIOXIDE
CARBON DIOXIDE
CARBON DIOXIDE

Figure 2-5: Chemical and Microbial Degradation Pathways of TCA (A = Abiotic, B = Biotic) (Modified From Vogel, 1994)

BENZENE


BENZENE
Ring Reduction
Ring Oxidation
CYCLOHEXENE
PHENOL
ALIPHATIC ACIDS
CH_4 . CH_4

TOLUENE

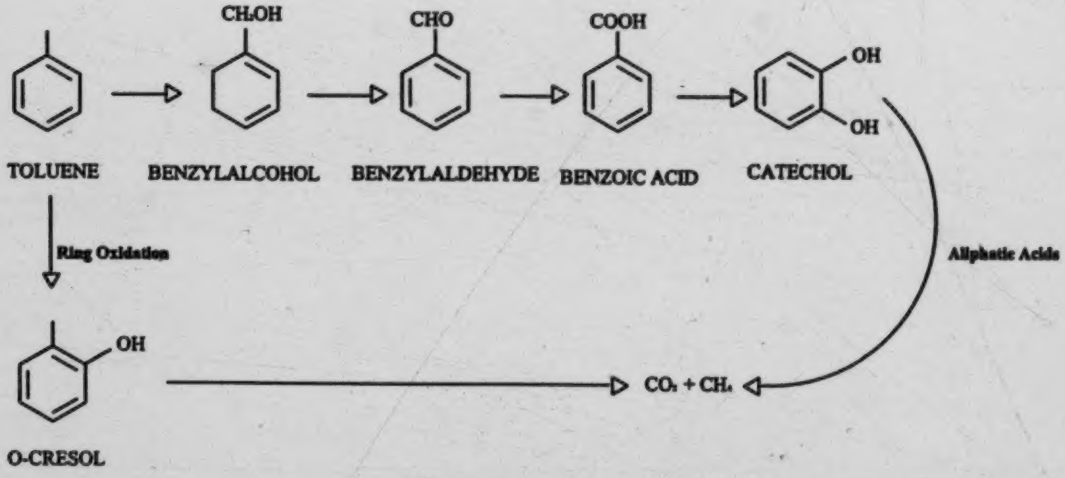

CH_2OH
CHO
COOH
OH
OH
TOLUENE
BENZYLALCOHOL
BENZYLALDEHYDE
BENZOIC ACID
CATECHOL
Ring Oxidation
Aliphatic Acids
OH
CO_2 + CH_4
O-CRESOL

Figure 2-6: Benzene and Toluene Biodegradation Under Methanogenic Conditions (Modified From Verschueren, 2000; Chapelle, 2001)

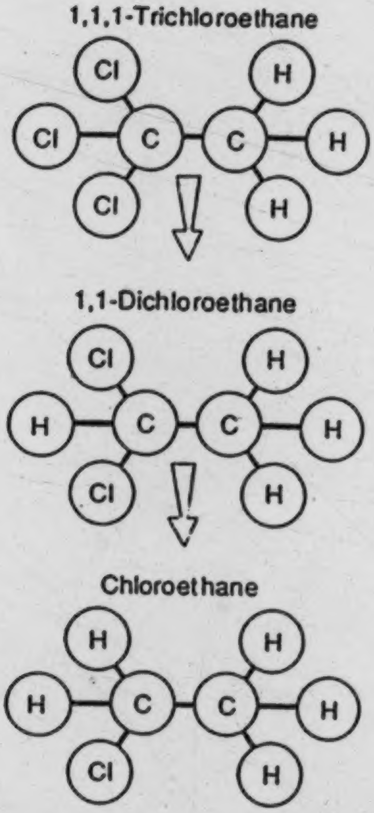

1,1,1-Trichloroethane
Cl
H
Cl
C
C
H
Cl
H
1,1-Dichloroethane
Cl
H
H
C
C
H
Cl
H
Chloroethane
H
H
H
C
C
H
Cl
H

Figure 2-7: Transformation of 1,1,1-TCA into Chloroethane (Modified From Weidemeier et al., 1998)

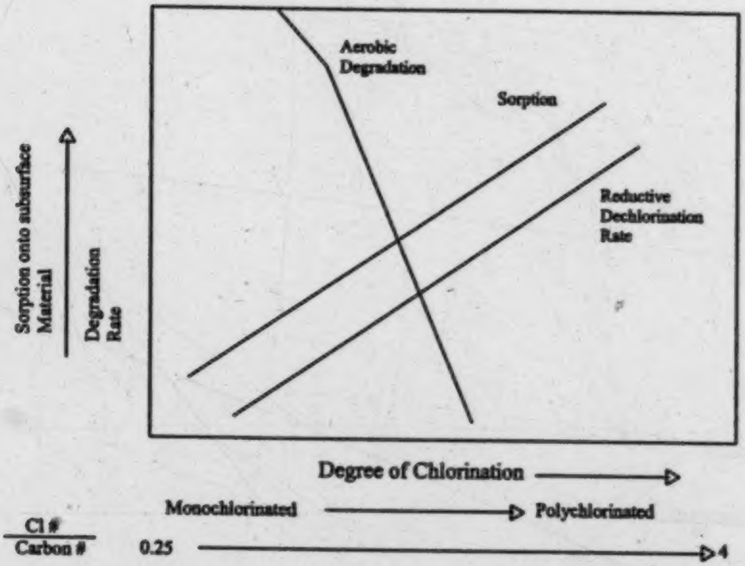


Figure 2-8: Relationships Between Degree of Chlorination and Anaerobic Reductive Dechlorination, Aerobic Degradation and Sorption Onto Subsurface Material (Modified From Vogel, 1994)

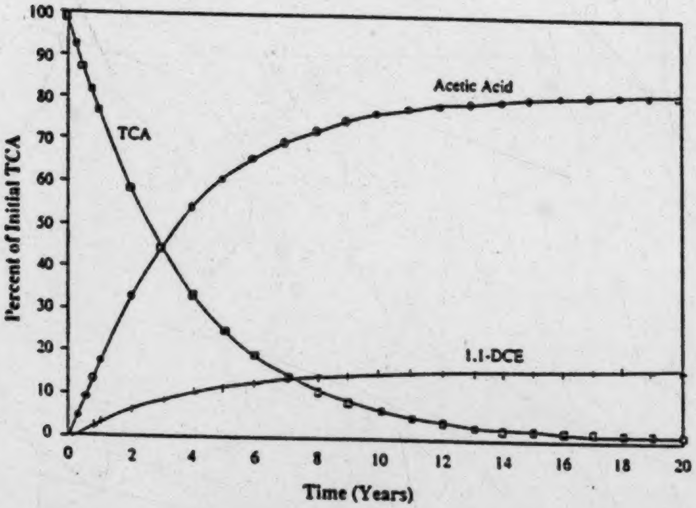


Figure 2-9: Distribution of TCA Degradation Products for Abiotic Chemical Degradation (Modified From Vogel, 1994)

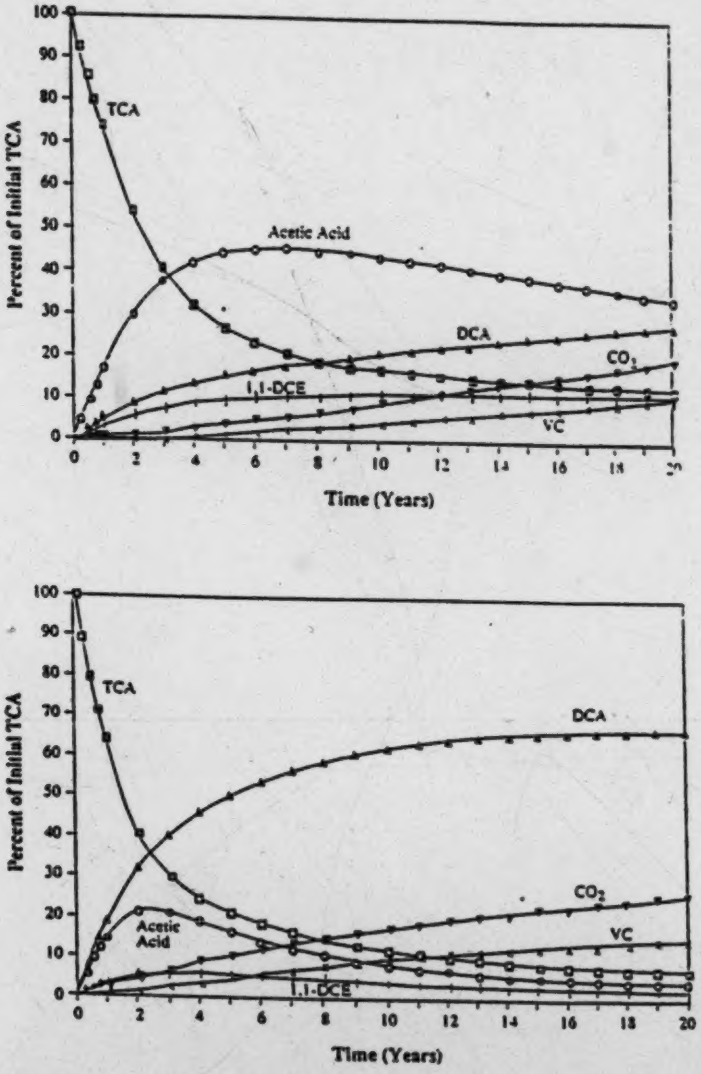


Figure 2-10: Distribution of Microbial and Chemical Degradation Products of TCA for (a) Lower Microbial Activity and (b) Higher Microbial Activity (Modified From Vogel, 1994)

3.0 DESCRIPTION OF SITE AND GEOLOGY

3.1 LOCATION OF SITE

The landfill site is located in CFB Cold Lake, Alberta. CFB Cold Lake is situated close to the community of Grand Centre, approximately 250 km northeast of Edmonton, and 10 km from the Alberta-Saskatchewan border. Figure 3-1 is a historical photo (1955) showing the location of the landfill site in relation to the rest of the base infrastructure. The study site is indicated on the photo.

3.2 SITE DESCRIPTION

The landfill is estimated to be approximately 450 by 1100 m in size. It is bordered on the south side by a runway and on the north to northeast side by a bog and then Marie Creek. The site now consists of relatively flat terrain with cut paths and small trees (spruce and poplar). Closer to Marie Creek and the boggy area are tall trees and thick brush. Figure 3-2 shows a map of the area showing the boundary of the landfill and the burial sites. There are no written records available to indicate what types of materials were buried, but interviews with Base personnel indicated that the site was previously the principal waste disposal area for all of CFB Cold Lake. Portions of the site appear to have been used to bury various degreasers and fuels. All dumping has ceased and the site has been filled and leveled. At some locations the soil and groundwater was found to contain elevated levels of chlorinated hydrocarbons and BTEX compounds, especially in the area of the drainage ditch and Well 7. Examination of groundwater from the bog also indicated a presence of TCA and DCA (RRMC, 1991). A risk assessment concluded that the groundwater, although contaminated, did not pose an immediate risk to human or environmental health. There was a concern, however, with the impact of surfacing groundwater. It appeared that the contaminants had not progressed beyond the leading edge of the bog (RRMC, 1991).

3.3 SITE STRATIGRAPHY

Overall, the landfill area is quite flat, although the Marie Creek valley is steep-sided. To the north east of the landfill, and on the top of the Marie Creek escarpment, is a gently sloping, land-locked bog characterized by sphagnum beds and low lying shrubs and evergreens. The drainage ditch from the storm sewer outfall extends into this area. The stratigraphy consists of fine to medium silty sand of about 2.5 m thickness (upper glaciofluvial sediments). A grey clay till of Grand Centre formation lies underneath the silty sand and acts as an aquitard. Figure 3-3 shows a typical geological section for the landfill site. Throughout the clay till there are disconnected seams of silty sand dispersed throughout the area. Beneath the clay till lies a silty sand layer to depths in excess of 17 m. The slopes between the bog and Marie Creek are wooded and provide drainage for the area.

Figure 3-1: Historical Photo of Old Landfill Site (1955) (Modified From RRMC, 1991)

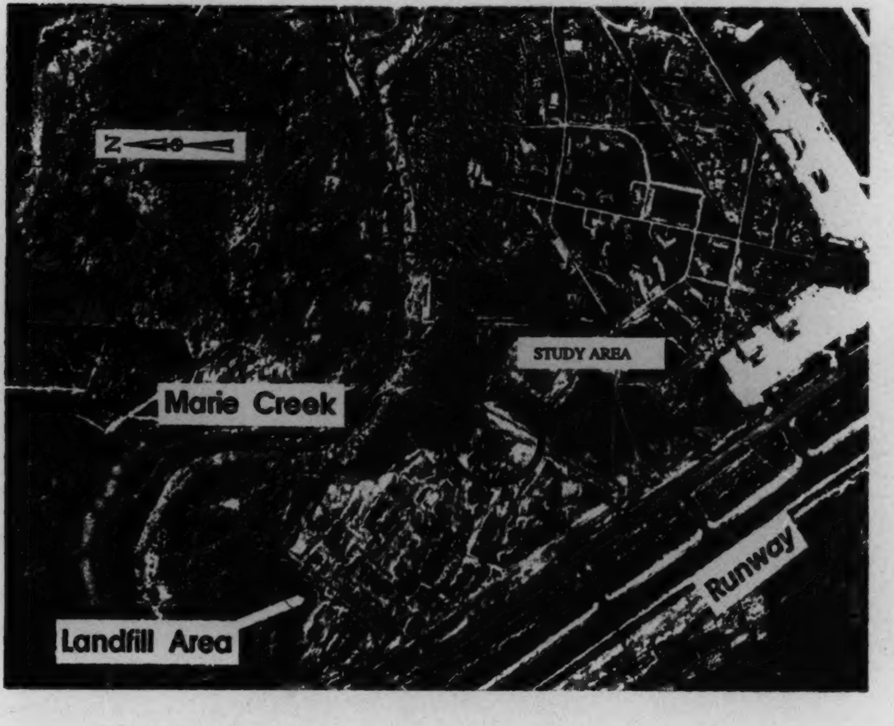
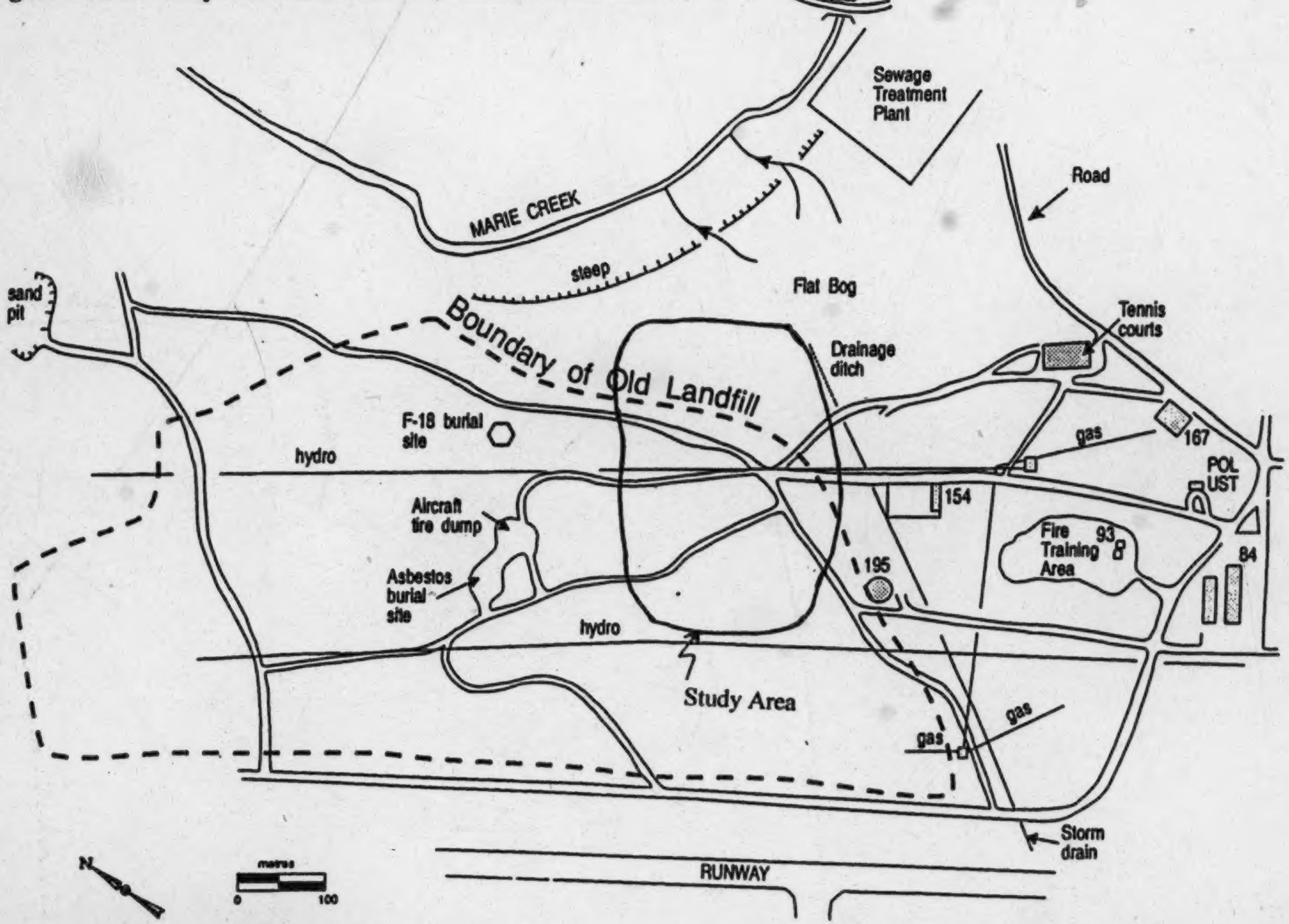
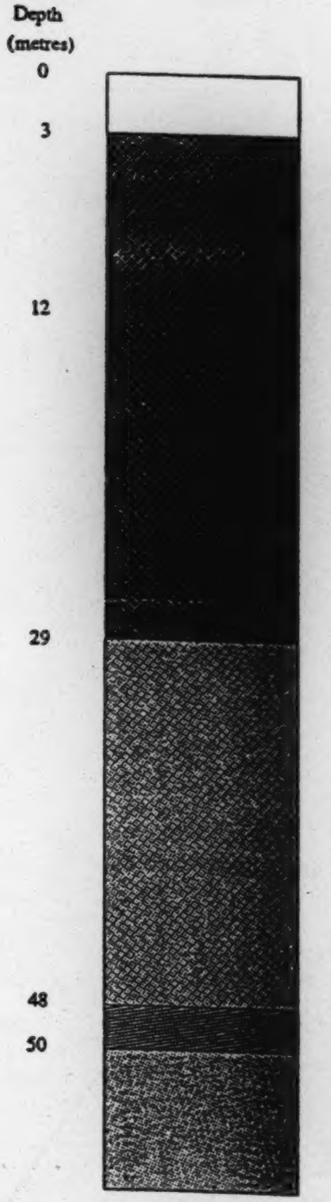

N
STUDY AREA
Marie Creek
Runway
Landfill Area

Figure 3-2: Boundary of Old Landfill Site (Modified From RRMC, 1991)


Sewage Treatment Plant
Road
MARIE CREEK
steep
Flat Bog
Tennis courts
sand pit
Boundary of Old Landfill
Drainage ditch
F-18 burial site
gas
167
POL UST
hydro
154
Aircraft tire dump
Fire Training Area
93
84
Asbestos burial site
195
hydro
Study Area
gas
gas
Storm drain
N
metres
0
100
RUNWAY

Map compiled from Site Record Dwg. L-C252-8429, updated from aerial photo A27209-214 and field observations.



Description

Glaciofluvial sediment - sand

Grand Centre Formation - Reita Lake Member: Clayey-sand diamicton; very coarse sand fraction is rich in igneous, metamorphic and quartz rock fragments; glacial sediment (till)

Marie Creek Formation - Unit 2: Sandy diamicton; very coarse sand fraction is rich in carbonate rocks fragments; glacial sediment (till)

Bonnyville Formation - Unit 2: Diamicton, sandy; very coarse sand fraction is rich in quartz fragments; glacial sediment (till)

Muriel Lake Formation: Sand and gravel; minor silt and clay; glaciofluvial sediment

Lea Park Formation: Dark grey shale; pale grey glauconitic, silty shale with ironstone concretions; marine

Figure 3-3: Geological Cross Section at Landfill Site (Modified From RRMC, 1991)

4.0 PROGRAM OF INVESTIGATION

This U of A investigation at the landfill site consisted of three parts:

- Site investigation;
- Assessment; and
- Microcosm studies

4.1 BACKGROUND

4.1.1 Previous Studies

4.1.1.1 1989 1 Construction Engineering Unit Report

In 1988, a hydrocarbon sheen was observed in the drainage ditch near the stormwater outfall and in the boggy area near Marie Creek. Environment Canada was aprised of the situation and conducted a preliminary assessment, analyzing surface and groundwater, soil, and sediment samples from the drainage ditch and Marie Creek. Their studies confirmed the presence of hydrocarbons near the ditch, but none in Marie Creek (RRMC, 1991).

In 1989, 1 Construction Engineering Unit (1 CEU) conducted field work which included drilling boreholes and installing monitoring wells, and collecting surface and subsurface soil and groundwater samples. Field work took place in two phases, 8-18 Aug 1989 and 2-4 October 1989. Figure 4-1 shows the location of the monitoring wells installed, Wells 1 to 11. They discovered that the waste disposal site is characterized by two distinct stratigraphies, a moderately permeable surface sand layer of approximately 2.5 to 3 m depth underlain by a till of about 7 m thickness. Underneath the till lies a silty sand of unknown depth. Figure 4-2 shows the geological cross-section. Groundwater in the sand layer was determined to be flowing in the northeasterly direction towards the boggy area near well 11. They also determined a lower sand layer beneath the till at a depth of approximately 7 meters, but their knowledge of this layer was limited. They did limited chemical analysis and determined the presence of contaminants including CAHs and monocyclic aromatic hydrocarbons (BTEX). They also determined the presence of a chemical that they assumed could be phosgene. They recommended a more detailed study of the contaminated site, a determination of feasibility of a site remediation alternative, and a monitoring program of contaminant migration through surface water between the contaminated area and Marie Creek. Their conclusion was that the bog and forested area between the site and Marie Creek was acting as a temporary buffer zone for the contaminants that, if it reached its capacity in the future, could allow contaminants to migrate into Marie Creek, and ultimately the Beaver River. It was also noted that such a contaminant migration would be violating Section 36 of the Fisheries Act. They also recommended further delineation of the contaminated area and evaluation of the feasibility of site restoration (RRMC, 1991).

4.1.1.2 1991 Royal Roads Military College Study

Royal Roads Military College conducted a follow-up study to the 1 CEU report. Their objective was to:

- evaluate environmental impact of the landfill and thereby establish an appropriate remediation program; and
- to train base personnel to monitor the landfill site.

They conducted an initial reconnaissance and sampling program and compared their own results to the findings described in the 1 CEU report. They also conducted a non-intrusive geophysical study of the area and installed and sampled additional monitoring wells. They interpreted the data resulting from all investigations and provided some recommendations for impact and remediation of the site.

Figure 4-3 shows the location of their first round of sampling sites, SW1 to SW8. The sites labeled SW represent the sites at which RRMC took surface water samples. SW1 was taken at Marie Creek, SW2 and SW3 were taken near the base of the steep slope down to Marie Creek, SW5 was taken at the flat bog, and SW9 was taken at the runway storm drainage ditch near Well 11. The results, shown in Table 4-1, indicate that surface water near Marie Creek had very low levels of contaminant (SW2 and SW3), whereas the drainage ditch and bog showed slightly higher levels (SW5 and SW9). Figure 4-4 shows the location of the new boreholes and monitoring wells associated with this study. TCA and DCA were detected only in wells 7 and 11. Table 4-2 shows the results from the first round of sampling for Well 7. Several contaminants were found in the well, including elevated levels of TCA and DCA.

Figure 4-5 and Figure 4-16 show the location of a second round of sampling sites including the monitoring wells (Wells 12 to 28) that were installed, from which groundwater samples were taken. Table 4-3 and 4-4 show the results of the second round of groundwater and surface water analyses. Samples SW13 to SW16 were taken in the wooded area beyond the bog, towards Marie Creek, to serve as an addition to the data collected in the first round. TCA and DCA were the only chlorinated aliphatics found and these were at very low levels. Typical detection limits for these compounds in water are approximately 1 µg/L in analyses performed by commercial laboratories. These results were compared to samples SW2 and SW3 of Table 4-3 and confirmed that very low levels of these CAHs were present in the wooded area beyond the bog. Table 4-4 shows that the largest concentrations of organic compounds in the upper aquifer were found in water sampled in the area extending from Well 17 to Well 27. The suspected source of contamination was an oil pit near Well 17 (RRMC, 1991).

There was general agreement between the RRMC results and the 1 CEU results, except that there was no indication of phosgene, as suspected by 1 CEU. The CAHs, 1,1,1-TCA and DCA might have been mistaken for phosgene since these compounds give mass spectra with fragmentation patterns similar to phosgene. BTEX, DCA, and TCA were the principal compounds of environmental concern. These compounds were found in both groundwater and surface water in the bog. They were also detected in the wooded area adjacent to Marie Creek, although with significantly lower concentrations. These target contaminants were not detected in the creek itself.

An electromagnetic survey was conducted by RRMC. The groundwater was determined to flow in a northeasterly direction by observing the salt leaching from a nearby salt storage building, confirming the 1 CEU conclusion.

Both 1 CEU and RRMC concluded that the groundwater surfaces just north of well 11. However, after both studies, there was still information lacking on the total extent of the contamination in the landfill. RRMC recommended to not solely rely on the bog "filtering capacity" as a solution for the contamination. Thus, they recommended installation of purge wells to remove the source.

4.1.1.3 1994-1997

In 1995, an orange colored slime was found in an area adjacent to the drainage ditch. The slime was sent to Norwest laboratories and they found a presence of bacteria and fungi in mucilaginous material. The predominant bacteria were later found to be *Pseudomonas* sp and *Aeromonas* hydrophilia.

In March, 1996, Dr. Carl Mendoza was asked to review the existing reports on the landfill site and to provide recommendations for its remediation. He indicated that the distribution of dissolved contamination was not likely to impact Marie Creek in the near future. He recommended that further studies be done to better delineate the light non-aqueous phase liquid (LNAPL) plume. Methods included detailed chemical analysis of groundwater and soil samples. He also suggested a number of options for remediating the source area, but emphasized that is was not to be done until the LNAPL plume was better defined (Mendoza, 1996).

On September 17, 1996, more samples were taken from the Royal Roads monitoring wells. The objective was to sample these wells prior to excavation of the suspected source area defined in the RRMC study. The samples were taken using dedicated Waterra™ foot valves or submersible turbine pumps. Table 4-5 shows the results of the sampling. The highest concentrations of TCA were found in Wells 7, 12, 17, and 27. Well 27 had the highest concentration (5140 µg/L). DCA was found in significant concentrations in the same wells where TCA was found in, but Well 7 had the highest concentration (2000 µg/L).

In 1996 (September 30 to October 8), the Construction Engineering Environmental cell excavated soil from the suspected source of contamination identified in the RRMC study and removed three areas of soil, each of 25 m x 32 m in size. They then removed an extra area that was approximately 16 m x 30 m. It appears from the draft report that the contaminated soil was removed to a depth of about 2 to 2.5 m.

4.1.1.4 An-Geo 1997 Investigation

In 1997, An-Geo Environmental Consultants Ltd. were hired to further investigate the former landfill site to characterize the stratigraphy and groundwater movement, and to determine the suitability of a funnel and gate remediation system. They installed 12 monitoring wells (Wells 201 to 212) and sampled from 14 of the existing wells, between July 30 and August 6, 1997. The installed wells are shown in Figure 4-6 and Figure 4-17. An-Geo confirmed the stratigraphy found by previous studies. They also conducted permeability tests (An-Geo, 1997).

They concluded that:

- the bog alone would not prevent influx of contaminants to Marie Creek and must not be regarded as the sole remedial measure for the site contamination;

- a funnel and gate system would not be feasible since groundwater flow rates across the study area were too high.
- Significant vertical variation in the water table over time with lack of information to define the flow fluctuation, and the discovery of free phase LNAPLs outside of the area designated for the funnel and gate system further supported their conclusion.

They recommended that the contaminant source be removed, either by excavation or pumping, to reduce chemical load to the groundwater and to enhance further remediation strategies for the groundwater contamination. Finally, they recommended ongoing monitoring to evaluate the performance of the recovery process (An-Geo, 1997).

4.1.1.5 1998 Pump and Treat

From December 14 to 19,1997, IWR Technologies Ltd. installed a multi-phase vacuum extraction to remove contaminated groundwater from wells 28, 27, 204, and 18. The multi-phase vacuum extraction took place from January to mid-March, 1998. Groundwater was passed through a separator and then through two vessels containing activated carbon. Finally, the water was passed through organic clay and then discharged to the bog. In February, 1998, results from the analysis of water were completed and the concentrations were 207 µg/L DCA and 113 µg/L TCA. The results showed that the water discharged into the bog was contaminated with high levels of TCA and DCA, which exceeded discharge requirements. Consequently, the system was demobilized and shut down (IWR, 1998).

4.1.1.6 Mullick 1998 Study

Anjum Mullick, a graduate student at the U of A, conducted a study (Mullick, 1998) to further delineate the plume and to evaluate intrinsic bioremediation as a remedial option. Existing monitoring wells were inspected and water levels taken. Two monitoring wells were installed (AH-07 and AH-08) and groundwater was sampled at several locations utilizing a Hydropunch® to conduct a more thorough groundwater analysis. Hydropunch sampling is described in Chapter 4.2.1.1. Figures 4-7 and 4-18 show the locations of the Hydropunch® samples (HP-5 to 15 and HP-21 to 26) and the auger holes. Soil samples were used for most probable number tests to evaluate the population of microbes in the soil at the site. The flow direction was determined to be relatively consistent with the 1 CEU and RRMC reports, flowing in a northeastern direction. The hydraulic gradient was determined to range from 9.23×10^{-3} to 1.3×10^{-2}, averaging 1.1×10^{-2}.

Additionally, nine slug tests were conducted to determine the hydraulic conductivity of the site. The average hydraulic conductivities for an anisotropy ratio of 1 and 1/3 were 7.1×10^{-5} and 7.9×10^{-5} m/s, respectively. The average of the two hydraulic conductivities was chosen to be 7.5×10^{-5} m/s. The average seepage velocity was determined to be approximately 76 m/year.

Microbial enumeration was conducted and the results are shown in Figures 4-8 and 4-9. During groundwater sampling, the pH, electrical conductivity, redox potential, temperature, and DO were measured while the groundwater was pumped into a flow-through cell with a bladder pump. The average pH was found to be 6.7. At a second visit to the site, it was found to be about 7.3. The average temperature was found to be approximately 8°C in the upper sand aquifer of about 2.5 m depth. The redox potential of the groundwater, measured with a platinum electrode probe, averaged –39 mV with a high of –19 mV and a low of –70 mV at Well 207. The groundwater was determined to be in a reducing environment since negative redox potentials indicate reductive conditions, which are associated with biodegradation processes. The electrical conductivity for the site was about 1489 µS/cm with a maximum of 9100 µS/cm at AH-07 and a minimum conductivity of 98 µS/cm at Well 608. The results of the electrical conductivity were inconclusive since a nearby salt storage building was leaching chloride ions and resulting in the high values. Finally, upgradient DO values ranged from 6.6 mg/L to 8.8 mg/L (considered background) near HP-5 and HP-21. However, towards the middle of the plume, the DO values approached 0.5 mg/L at Wells 12 and 28. The upgradient methane concentrations were non-detectable, but towards the middle of the plume the concentrations reached a maximum of 1.0 mg/L at Well 27.

Table 4-6 shows observed electron acceptor (geochemistry) and contaminant concentrations. Figure 4-10 shows the areas of aerobic and anaerobic conditions. Figure 4-11 shows the interpretation of the electron acceptor utilization. Figure 4-12 shows the distribution of TCA in the area. Figure 4-13 shows the distribution of DCA, and Figure 4-14 shows the distribution of BTEX.

Computer modeling was done using the BIOCHLOR program. Table 4-7 shows three possible cases analyzed and the results obtained. An expected biodegradation rate of TCA utilized was 1.0 yr^{-1}, with a maximum of 2 yr^{-1} and a minimum rate of 0.23 yr^{-1}. It was concluded that there was significant evidence for intrinsic bioremediation of BTEX and CAHs on site, despite the cold groundwater temperatures. The report recommendations were:

- To determine more information about the original source (near Well 17 and 12) and to examine the possible existence of a second source, near well 27, by looking for free-product perched atop the clay till;
- to further delineate the plume by increasing sampling downgradient to properly define the lateral extent of the plume; and
- to continue long-term monitoring.

4.1.2 Purpose of Further Investigation

There was sufficient uncertainty in the results of the Mullick (1998) study that additional data was needed to better delineate the extent of the plume and the presence and extent of the second source near well 27. The location of the non-detectable contour of contamination at the downstream (northeast) end of the plume was required to determine the plume extent and to develop an adequate groundwater fate and transport model. Furthermore, additional data would show the fluctuations of the groundwater table and contamination concentrations.

4.2 METHODOLOGY

4.2.1 Field Sampling Program Methodology

Additional data, gathered in 1999, was focussed around the second source at Well 27, a zone of high concentration. Therefore the area of investigation remained close to the existing boreholes and data. The critical area of concern was the source location and areas of insufficient data availability for proper delineation of the plume.

Based on previous contour plots of concentrations of TCA, DCA, and BTEX, a new drilling program was created in which Hydropunch® samples were obtained in areas that lacked data or that had uncertainty. Additionally, existing monitoring wells were sampled. All new and existing sampling points are shown in Figure 4-18.

4.2.1.1 Hydropunch® Groundwater Sampling

Hydropunch® samples were obtained at 19 locations in November, 1999, shown in Figure 4-15. The results are discussed in Section 6.0. In Hydropunch® sampling, a 50 mm diameter drill rod is pushed into the ground with the 1.2 m long sampling screen contained in the bottom section and capped with a disposable conical tip. The Hydropunch® utilizes an air-tight and water-tight sealed intake screen and sample chamber that is isolated from the surrounding environment as the tool is advanced. The surface of the Hydropunch® is designed to prevent the downward transport of the contamination as the tool is advanced; it cleans itself as the soil particles are displaced at the side. The tight seal created as the soil is displaced and compacted allows the collection of a discrete sample from a specific depth (Weidemeier et al., 1995).

The depths of the Hydropunch® samples were determined by a previous measurement of groundwater levels. The top of the screen was set at approximately 0.60 m to 0.90 m below the groundwater table. The rod was then withdrawn approximately 0.6 m to expose a screen. A 19 mm Waterra™ valve with a Teflon lined tube was used to sample the groundwater from within the Hydropunch® for each location. Figure 4-21 shows the drill rig that was used to push the Hydropunch® into the ground and the Teflon lined tube that was used to sample the groundwater. The water was pumped into a flow-through cell (a modified Thermos™ with a lid in which probes from various meters were inserted). From the flow-through cell, measured parameters included pH, electrical conductivity, dissolved oxygen, temperature, and redox potential. Figure 4-22 shows the flow-through cell used to take chemical measurements. The handheld meters used were the LaMotte DO 4000 Dissolved Oxygen Meter, the Oakton WD-35615-series pH/mV/temperature meter, and the Oakton WD-35607-30 Conductivity meter. The meters were calibrated frequently, whenever possible, to ensure quality control. The redox potential meter was malfunctioning and the values could not be relied upon. From each Hydropunch® test hole, samples were sent to Enviro-Test laboratories for analysis of volatile organic compounds (VOC), Routine Water Chemistry including pH, bicarbonate (HCO_3), calcium (Ca), carbonate (CO_3), chloride (Cl), conductivity, hardness, hydroxide (OH), magnesium (Mg), potassium (K), Sodium (Na), total dissolved solids (TDS) and total alkalinity; terminal electron acceptors including nitrate (NO_3) + nitrite (NO_2) = N and sulfate (SO_4), and Total Organic Carbon (TOC). Table 4-8 shows the groundwater sampling preservation and requirements. Included in the VOC analysis was TCA, 1,2-DCA, DCA, 1,2-DCB, 1,3-DCB, and 1,4-DCB and BTEX. Included in the Routine Water analysis were sulfate, nitrate, iron and manganese. These parameters would provide an indication of the electron accepting conditions of the plume. The Enviro-Test analyses were performed according to EPA methods. These methods are included in Appendix A.

4.2.1.2 Well Sampling

Existing wells were sampled in November, 1999, to provide additional information for the site. A Well Wizard bladder pump was used to obtain the water from these wells. The Well Wizard was operated at a purge rate of approximately 500 mL/min. and the depth of the sampling port was approximately 1 m below the water table. Three well volumes were purged before sampling and measuring pH, electrical conductivity (EC), reduction-oxidation potential (redox potential), temperature, and dissolved oxygen (DO). Care was taken not to aerate the water sample while the samples were obtained, since DO and redox potential values are affected by aeration.

Wells that could not produce enough water to use the bladder pump were sampled using a bailer. For these wells, a downhole DO measurement was taken before purging and sampling. The bailer consisted of an open-ended plastic tube containing a ball that rested against a sealing ring at the bottom of the tube. When the tube was lowered down the well, water entered the bailer and rose through it. At the required sampling depth the bailer was lifted and the ball sealed against the ring under the weight of a column of groundwater. Samples were analyzed for the same analytes as the Hydropunch® samples.

4.2.1.3 Auger Holes Near Well 27 and Well N

The purpose of auger holes was to provide soil for the microcosm tests and to determine concentrations of contaminants in soils at two critical sites. Solid stem augering took place approximately 1.5 m upgradient of well 27, 0.7 m east of well 27, and 4.6 m downgradient of well 27. Figure 4-23 shows a photo of the solid stem auger used for sampling. This augering was done to obtain soil samples from within the sand layer immediately below the water table, in the middle of the sand aquifer, and at the base of the aquifer. These samples were taken to determine the exact location of the free product in the sand layer, if any. If the free product were pooled on top of the till, it would indicate that the area near well 27 was a source of contamination, something that had been suspected after the Mullick (1998) investigation.

Next, solid stem augering was used, near well 27 and well N, to obtain soil samples in 1 Litre glass mason jars for microcosm batch testing. These samples were capped with groundwater and were kept in the dark at 4°C in closed coolers until used for the microcosm tests, to inhibit microbiological activity.

4.2.1.4 Field Sample Quality Control

Duplicate samples, rinsate and field blanks were obtained throughout the drilling and sampling program for quality control. Field blanks are used to ensure that volatiles in the air were not contaminating samples. The blanks were obtained by exposing vials of distilled water near the sampling location, for a few minutes, and then capping them and analyzing for VOC. Rinsate blanks provide checks on the cleaning quality of the equipment, to ensure that the equipment was not contaminating the samples. After the equipment was cleaned thoroughly, distilled water was poured through the sampling system and into the vials, which were also analyzed for VOC. Duplicate samples were taken at a number of the contaminated wells for quality check of the ETL analysis and to examine variability of samples.

4.2.2 Laboratory Testing Program Methodology

4.2.2.1 Methane Analysis

Methane analyses were done in Dr. Fedorak's laboratory in microbiology at U of A with the aid of his student, Ms. Holowenko. The dissolved methane analyses were done utilizing a gas chromatograph with a flame ionization detector. The sample preparation was done according to Kampbell et al. (1989) and Kampbell et al. (1998), except that nitrogen instead of helium was used to create the headspace in each sample since no helium was available for use. Each 40 mL vial of groundwater sample was held upside down with a clamp. A tube with a needle attachment was used to inject nitrogen gas into the sample while a syringe was used simultaneously to collect the excess groundwater until a 4 mL headspace was created. The amount of water collected from the sample depended on the amount of headspace that originally existed in the sample. Ideally, the original sample would contain no headspace because the presence of headspace would allow the methane to volatilize into a gas from the groundwater. Water was removed from the sample bottle using the method outlined by Kampbell et al. (1989) and the headspace that was created was analysed for methane. Table 4-9 shows the measured methane concentrations for the site. Detailed calculations and gas chromatograph specifications, and procedures are given in Appendix B.

4.2.2.2 Microcosm Testing Procedure

Microcosm studies were conducted to determine the rates at which the indigenous microorganisms at the site are capable of degrading contaminants in an anaerobic environment. The purpose of the microcosm studies was to develop a first order rate constant and to attempt to physically verify the processes involved in the degradation of the contaminants. A gas chromatograph with flame ionization detector (FID) was used for measuring the amount of contaminant in the microcosm test vials. The chromatograph was calibrated and blanks and prepared standards were analysed consistently to ensure quality results. The gas chromatograph specifications, details of the gas chromatograph calibration, calibration test results, and quality control procedures are included in Appendix C.

The detailed procedure for the microcosms is contained in Appendix E. Due to difficulties encountered with the gas chromatograph, there were delays in starting the microcosm study. Consequently the soil and groundwater that were sampled for the microcosm tests were stored at approximately 4°C for almost two and a half months. Generally, approximately 240 microcosm vials (30 mL) consisting of 15% soil, 42.5% ground water, and 52.5% distilled water (by volume) were prepared, 120 for an upstream site, near Well N, and 120 for a downstream site, near Well 27. Approximately 80 negative controls were prepared, 40 consisting of the same ratio of soil and ground water, and 40 consisting of only ground water. The negative controls were sterilized by autoclaving batches of soil and groundwater three consecutive times at approximately 121°C and transferring the components into autoclaved vials under nitrogen gas flushing. The microcosms were sacrificed in triplicate on each sampling event and single negative control samples were analysed every second sampling event.

After the October 28 sampling event, it was found that the negative controls contained almost non-detectable amounts of the compounds of concern (TCA, DCA). The remaining negative controls (which were yet to be analyzed) were then spiked with sterilized known concentrations of TCA, DCA, 1,3-DCB, 1,4-DCB, and 1,2-DCB. From all the microcosms, the concentrations were plotted versus time and examined for trends. Finally, before the sampling events in December, the 10°C incubator was accidentally switched to –10°C for a day, freezing the samples. The results of the microcosm tests are presented in Chapter 5 and discussed in Chapter 6.

Table 4-1: RRMC Surface Water Samples (Modified From RRMC, 1991)

Sample	1,1-Dichloroethane µg/L (ppb)	1,1,1-Trichloroethane µg/L (ppb)
SW2	2.6	< 1.0
SW3	10.3	< 1.0 trace
SW5	101	6.2
SW9	2	14

Table 4-2: First Round Groundwater Analysis of Well 7 (Modified From RRMC, 1991)

Compound	Concentration (µg/L; ppb)
chlorethane	< 100
1,1-dichloroethane	1800
1,1,1,-trichloroethane	1800
benzene	520
toluene	1300
ethylbenzene	110
m and p-xylene	1100
o-xylene	1200
1,2-dichlorobenzene	46
other aromatic compounds	1800
cis-1,2-dichloroethylene	48
phenol	11

Table 4-3: RRMC Second Round Surface Water Analysis (Modified From RRMC, 1991)

Sample	1,1,-Dichloroethane µg/L (ppb)	1,1,1-Trichloroethane µg/L (ppb)
SW13	0.2	0.7
SW14	2.1	1.4
SW15	0.9	< 0.2
SW16	3.6	0.3

Table 4-4: RRMC Second Round Groundwater Analysis Results (Modified From RRMC, 1991)

Site	Benzene (μg/L)	Toluene (μg/L)	Ethylbenzene (μg/L)	Xylenes (μg/L)	Σ BTEX (μg/L)	1,1,1-TCA (μg/L)	1,1-DCA (μg/L)
Well 7	510	1173	200	1510	3393	625	4160
Well 12	1490	3600	500	4170	9760	850	340
Well 16B	590	810	61	460	1921	25	460
Well 17	3270	6715	590	4080	14655	2370	590
Well 18	<1.0	<1.0	<1.0	<1.0	0	2.3	0.2
Well 23	730	2460	230	3370	6790	2580	650
Well 27	3160	5300	300	3000	11760	1450	4620
Well 28	30	52	320	320	722	165	45

Table 4-5: 1996 Monitor Well Sampling (Modified from Pedersen, 1996)

	Benzene (mg/L)	Toluene (mg/L)	Ethylbenzene (mg/L)	Xylenes (mg/L)	Σ BTEX (mg/L)	1,1,1-TCA (µg/L)	1,1-DCA (µg/L)
Site							
Well 7	<0.050	0.55	3.41	37	40.96	697	2000
Well 12	1.08	2.7	0.052	2.86	6.69	830	420
Well 14	<0.001	<0.001	<0.001	<0.001	0	<1.0	<1.0
Well 16B	0.229	0.312	<0.010	0.696	1.24	5	1353
Well 17	0.051	0.093	<0.01	2.06	2.2	639	107
Well 26	<0.001	<0.001	<0.001	<0.001	0	<1.0	2
Well 27	1.19	2.91	0.338	2.9	7.34	5140	1820
Well 28	<0.001	0.002	0.001	0.002	0.005	51	8

Table 4-6: Groundwater Analysis (Mullick, 1999)

		WATER NUTRIENTS		WATER CHEMISTRY				NON-HALOGENTATED AROMATICS					VOLATILE ORGANIC COMPOUNDS			
WELL SITE	DATE	$NO_3 + NO_2$	SO_4	S^{2-}	TOC	CH_4	Fe^{2+}	Benzene	Toluene	Ethylbenzene	Xylenes	Σ BTEX	1,1,1-TCA	1,1-DCA	DCBs	VC
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(mg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
4	17-Jun-98							< 1.0	1	< 1.0	< 1.0	0.001	1	< 1.0	< 1.0	< 2.0
5	14-Aug-98	< 0.05	12.3	< 0.002	11		8.8	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
7	16-Aug-98							900	650	25	1540	3.115	< 1.0	35	67	< 10.0
9	10-Aug-98	0.1	0.9	< 0.002	6		0.4	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
12	10-Aug-98	< 0.2	< 0.5	< 0.002	67		126	4500	4500	300	2000	11.3	1100	55	96	< 2.0
13	15-Aug-98	0.08	23.7	< 0.002	11		< 0.1	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
14	7-Aug-98	< 0.05	< 0.5	0.023	25		44.1	<0.1	1.1	0.2	3.8	0.0051	0.5	0.1	< 0.1	< 0.2
17	16-Jun-98							760	4100	290	2800	7.95	940	53	28	< 2
17	10-Aug-98	< 0.2	8.3	< 0.002	259		94.2	1700	5700	330	3700	11.43	2800	< 60.0	61	< 2.0
18	16-Jun-98							< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 1.0	< 1.0	< 2.0
26	10-Aug-98	< 0.05	20.6	< 0.002	10		< 0.1	< 1.0	< 4.0	< 1.0	< 5.0	< 0.005	< 3.0	1	< 3.0	< 2.0
27	17-Jun-98							1400	4500	850	3550	10.3	10000	150	54	4
28	16-Jun-98							3	40	41	1300	1.384	42	34	40	< 2
28	10-Aug-98	< 0.2	4	< 0.002	44		107	< 1.0	37	17	810	0.864	84	25	53	< 2.0
201	13-Aug-98							< 270	9200	2400	15100	26.7	< 270	< 540	< 270	< 540
202	17-Jun-98							1	14	3	23	0.041	2	< 2.0	< 1.0	< 2.0
203	8-Aug-98	0.93	29.8	0.003	8		1.8	< 1.0	< 1.0	< 1.0	5	0.005	< 1.0	< 2.0	< 1.0	< 2.0
204	3-Oct-98	< 0.2	13.9	0.002			202	19	2500	90	3100	5.709	8800	< 2.0	96	< 2.0
205	16-Jun-98							98	160	9	880	1.147	290	420	53	< 2
Duplicate 205	16-Jun-98							98	160	7	917	1.182	300	430	52	< 2
206	3-Oct-98	< 0.2	9.9	< 0.002			96.7	130	200	15	900	1.245	< 2.0	< 2.0	71	2
207	8-Aug-98	< 0.005	29.7	< 0.002	10		0.9	2	13	1	11	0.027	< 1.0	< 1.0	< 1.0	< 2.0
Duplicate 207	8-Aug-99	< 0.005	28.4	< 0.002	9		1	2.4	13	0.9	14	0.0303	< 1.0	< 1.0	< 1.0	< 2.0
211	16-Jun-98							< 1.0	2	< 1.0	2	0.004	< 1.0	< 1.0	< 1.0	< 2.0
608	8-Aug-98	0.06	1.8	< 0.002	7		0.1	< 1.0	< 1.0	< 1.0	7	0.007	< 1.0	< 2.0	< 1.0	< 2.0
16A	16-Jun-98							< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 1.0	< 1.0	< 2.0
16B	8-Aug-98	< 0.05	0.6	< 0.002	28		25.7	86	210	< 10	526	0.822	< 10	290	24	< 100
AH-07	3-Oct-98	< 0.2	25	0.003			217	1300	680	43	3900	5.923	3200	120	109	< 2.0
AH-08	3-Oct-98	< 0.05	21.9	< 0.002			9	14	29	< 2.0	560	0.603	29	< 2.0	38	< 2.0
Drainage Ditch	16-Jun-98							< 1.0	2	< 1.0	12	0.014	< 1.0	< 2.0	< 1.0	< 2.0
HP-01	12-Aug-98				9											
HP-04	13-Aug-98	< 0.05	11.1	< 0.002	4		98									
HP-05	13-Aug-98	10.7	6.4	< 0.002	30		< 0.1	< 1.0	< 1.0	< 1.0	< 1.0	<0.001	< 1.0	< 2.0	< 1.0	< 2.0
HP-06	14-Aug-98						< 0.1	< 1.0	< 1.0	< 1.0	< 1.0	<0.002	< 1.0	< 2.0	< 1.0	< 2.0
HP-07	14-Aug-98	1.56	39.1	< 0.002	27		< 0.1	< 1.0	2	< 1.0	< 1.0	0.002	< 1.0	< 2.0	< 1.0	< 2.0
HP-08	14-Aug-98	< 0.2	10.1	0.011	22		81.8	47	4000	190	5500	9.737	3600	140	123	< 2.0
Duplicate HP-08	14-Aug-99	<0.2	9.9	0.011	21		80.2	45	3900	190	5700	9.835	3850	135	120	< 2.0
HP-09	14-Aug-98	< 0.2	4.9	< 0.002	32		409	210	1600	< 10	3800	5.61	2700	< 20	< 49	< 20
HP-10	14-Aug-98	< 0.05	3.7	0.023	25		119	< 1.0	35	41	10800	10.876	39	< 2.0	43	< 2.0
HP-11	14-Aug-98	1.02	3.9	< 0.002	18		< 0.1	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
HP-12	14-Aug-98	< 0.005	3.4	< 0.002	22		129									
HP-13	14-Aug-98	1.18	10	0.007	11		14	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
Duplicate HP-13	14-Aug-98	1.16	9.5	0.003	10.3		11.6	< 1.0	< 1.0	< 1.0	< 1.0	< 0.002	< 1.0	< 2.0	< 1.0	< 2.0
HP-14	15-Aug-98	< 0.05	< 0.5	0.004	28		101	< 1.0	1	< 1.0	4	0.005	< 1.0	< 2.0	< 1.0	< 2.0
HP-15	15-Aug-98	< 0.05	1.1	0.003	44		88.8	< 1.0	< 60.0	< 50.0	< 50.0	< 0.06	53	< 2.0	< 50.0	< 2.0
HP-22	5-Oct-98	< 0.2	4.7	0.01			122	< 10	38	< 10	55	0.093	< 10	< 20	< 10	< 20
HP-23	5-Oct-98	< 0.2	7	< 0.002			233	210	180	33	610	1.033	< 1.0	< 30.0	30	< 2.0
HP-24	5-Oct-98	< 0.2	13	0.007			449	490	3100	230	2600	6.42	680	2600	76	< 2.0
HP-25	5-Oct-98	< 0.2	12.4	0.003			183	10	360	59	1010	1.439	< 2.0	1	73	< 2.0
HP-26	5-Oct-98	< 0.2	10.5	0.011			361	1200	3800	260	4800	10.06	< 2.0	3500	125	< 2.0
Duplicate HP-26	5-Oct-98	< 0.2	9.8	0.009			380	1200	3750	270	4800	10.02	< 2.0	3200	115	< 2.0
Manhole	16-Jun-98							< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
SW1	10-Aug-98	< 0.005	1.4	0.003	11		< 0.1	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
SW2	10-Aug-98			0.003	19		1.9	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
SW3	15-Aug-98			0.002			526	< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 2.0	< 1.0	< 2.0
Rinsate Blank	16-Jun-98							< 1.0	1	< 1.0	< 1.0	< 0.001	< 1.0	< 1.0	< 1.0	< 2.0
Rinsate Blank	14-Aug-98							< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 1.0	< 1.0	< 2.0
Rinsate Blank	3-Oct-98							< 1.0	< 1.0	< 1.0	< 1.0	< 0.001	< 1.0	< 1.0	< 1.0	< 2.0

Table 4-7: Description of Three Possible Field Cases From Biochlor Modeling (Modified From Mullick, 1999)

Case	Seepage Velocity (m/yr)	Longitudinal Dispersivity (m)	Transverse Dispersivity (m)	Vertical Dispersivity (m)	Biodegradation Rate (yr^{-1})
Worst	100	100	0.1	1×10^{-99}	0.23
Best	30	1	0.01	1×10^{-99}	2.00
Expected	50	1	0.01	1×10^{-99}	1.00

Table 4-8: Groundwater Preservation Summary (November, 1999)

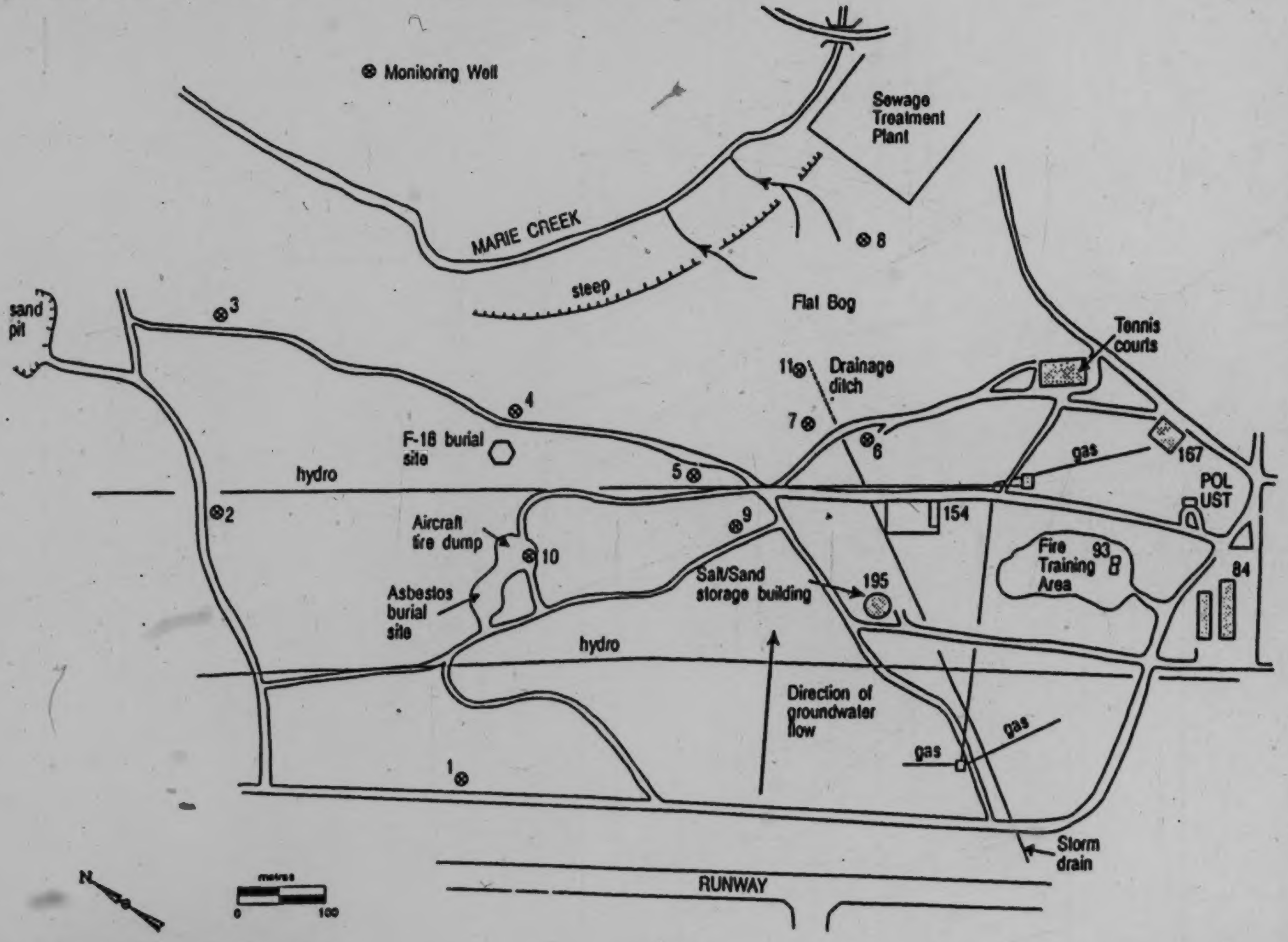
Analyte	Container Volume and Type	Number	Preservative
Routine (NO_3^-, NO_2, SO_4^{2-})	500 mL polyethylene	1	None added
TOC	100 mL amber, linerless cap	1	1 mL 1:1 sulfuric acid
VOC	40 mL glass vial	3	Sodium thiosulfate
Fe^{2+}	150 mL polyethylene	1	0.4 mL 6N HCl
Methane	40 mL glass vial	1	1 mL 6M HCl

Table 4-9: Groundwater Electron Acceptor and Microbial Byproduct Concentrations (November, 1999)

	NO_3+NO_2 (mg/L)	SO_4 (mg/L)	Mn (mg/L)	Fe^{2+} (mg/L)	TOC (mg/L)	CH_4 (mg/L)
Site						
Well 13	20.7	15.2	0.18	< 0.06	10	
Well 17	< 0.5	27.2	13.6	102	467	
Well 27	< 0.5	12.7	5.62	94.8	126	0.4
Well 27 Duplicate	< 0.5	18.1	5.73	92.3	129	
Well 27 Rinsate	< 0.1	0.5	< 0.02	0.07	2	
Well 27 Field	< 0.1	< 0.5	< 0.02	< 0.06	1	
Well 204	< 0.5	11.9	5.26	80	70	
Well 205	< 0.5	21.1	31.6	265	171	1.5
Well 206	< 0.5	19.9	21.8	174	160	
Well 210	< 0.5	8.3	6.75	60	80	
Well 211	2.4	10.2	0.12	0.98	5	ND
AH-7	< 0.6	26.7	10.1	128	242	1.7
HP-27	< 0.5	29	14.6	271	325	0.6
HP-28	< 0.5	29.6	20.8	262	599	1.4
HP-28 Duplicate	< 0.5	33.7	21.2	252	577	
HP-29	< 0.1	17.5	6.31	48.5	7	
HP-30	< 0.1	11.3	20.8	119	16	ND
HP-31	< 0.1	3.5	3.05	5.54	13	0.8
HP-32	< 0.1	6.5	8.46	174	34	1.2
HP-32 Rinsate	0.8	2.6	< 0.02	< 0.06	133	
HP-32 Field	< 0.1	0.6	< 0.02	< 0.06	< 1	
HP-33	< 0.1	8.7	3.48	27.2	61	0.2
HP-34	< 0.5	18.2	17.7	201	167	2.5
HP-35	< 0.1	5.9	8.6	160	14	3.3
HP-36	< 0.5	25.2	19.1	334	283	0.3
HP-37	< 0.5	13.3	12.9	140	97	0.4
HP-38	< 0.5	23.6	12.9	214	88	ND
HP-39	< 0.5	28	10.2	149	89	ND
HP-39 Duplicate	< 0.5	26.2	11.6	177	88	
HP-40	< 0.5	17.6	16.4	122	8	0.4
HP-41	< 0.5	25.6	18.8	243	132	0.2
HP-42	< 0.5	20.8	12	165	182	0.2
HP-43	< 0.5	17.1	7.75	194	110	1.6
HP-44	< 0.5	12.6	20.9	388	80	0.8
HP-45	< 0.5	37.4	22.3	594	187	1.6
HP-45 Rinsate	< 0.1	1.5	< 0.02	0.07	2	
HP-45 Field	< 0.1	< 0.5	< 0.02	< 0.06	1	
Well N	< 0.5	20.1	7.03	69.8	?	1.2

1. Rinsate blanks = distilled water collected by rinsing already cleaned sampling equipm
(to check efficiency of cleaning system)
2. Field blanks = distilled water collected in sample bottles and left open to the atmosph
near the sampling sites (to check effect of volatilization on sampling)
3. ND = non-detect
4. The symbol "<" indicates value less than detection limit

Figure 4-1: Location of 1 CEU Monitoring Wells (1-11) (Modified From RRMC, 1991)


⊗ Monitoring Well
Sewage Treatment Plant
MARIE CREEK
steep
8
Flat Bog
sand pit
3
11
Drainage ditch
Tennis courts
7
4
6
F-18 burial site
gas
167
5
hydro
POL UST
2
9
154
Aircraft fire dump
10
Fire Training Area
93
84
Asbestos burial site
Salt/Sand storage building
195
hydro
Direction of groundwater flow
gas
gas
1
Storm drain
RUNWAY
N
metres
0
100

Map compiled from Site Record Dwg. L-C252-8429, updated from aerial photo A27209-214 and field observations.

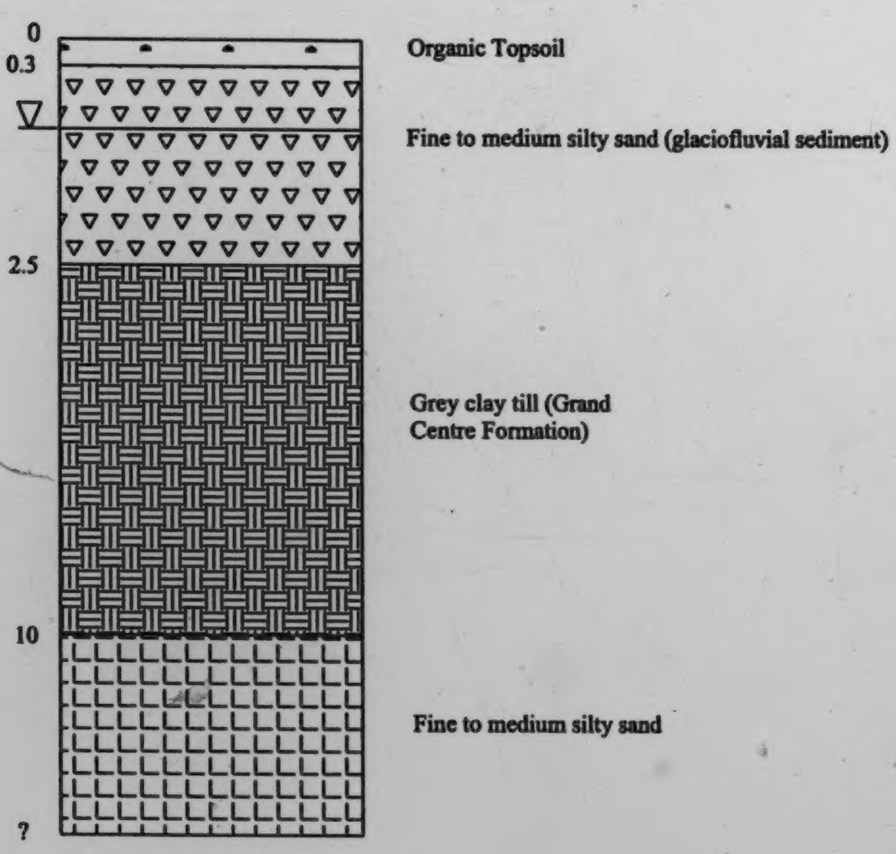
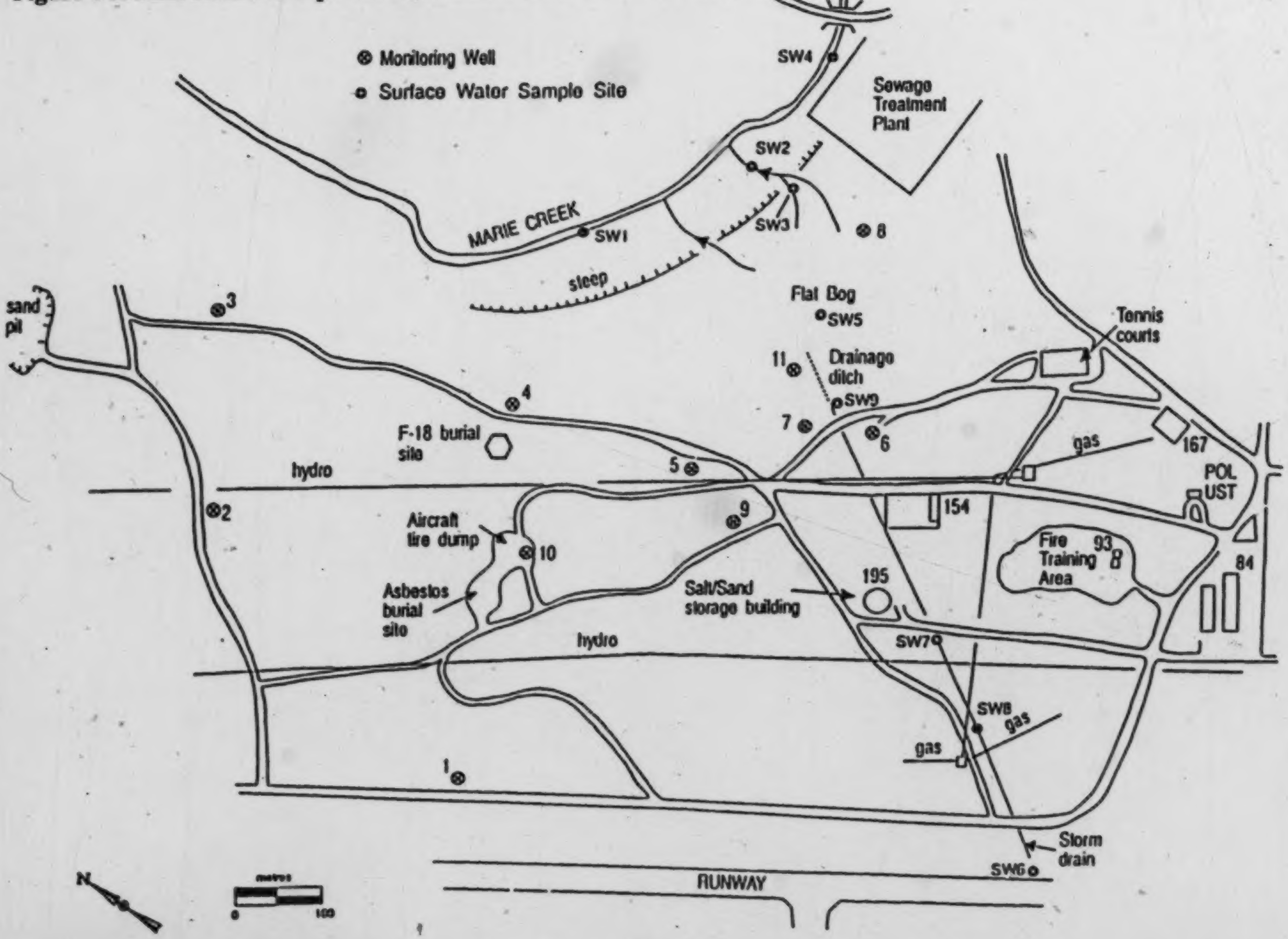
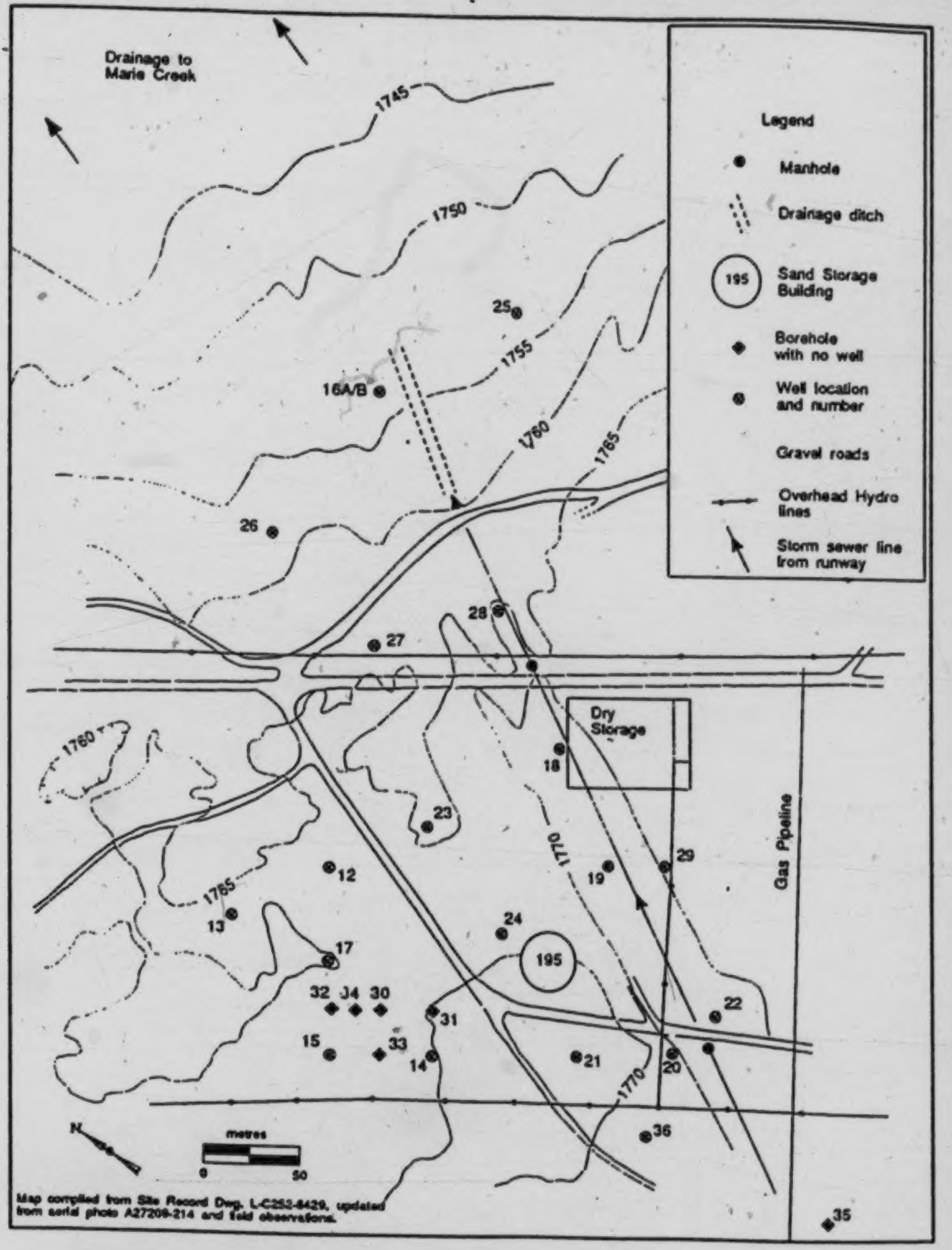

0
0.3
2.5
10
?
Organic Topsoil
Fine to medium silty sand (glaciofluvial sediment)
Grey clay till (Grand Centre Formation)
Fine to medium silty sand

Figure 4-2: Typical Geological Cross-Section (Modified From RRMC, 1991)

Figure 4-3: First Round Sample Sites (Modified From RRMC, 1991)


⊗ Monitoring Well
○ Surface Water Sample Site
SW4
Sewage Treatment Plant
SW2
SW3
⊗ 8
MARIE CREEK
SW1
steep
Flat Bog
SW5
11 ⊗
Drainage ditch
SW9
sand pit
⊗ 3
⊗ 4
F-18 burial site
7 ⊗
⊗ 6
Tennis courts
167
gas
POL UST
5 ⊗
hydro
⊗ 2
⊗ 9
154
Aircraft tire dump
⊗ 10
Fire Training Area
93
84
Asbestos burial site
Salt/Sand storage building
195
hydro
SW7
SW8
gas
gas
1 ⊗
Storm drain
SW6
RUNWAY
N
metres
0
100

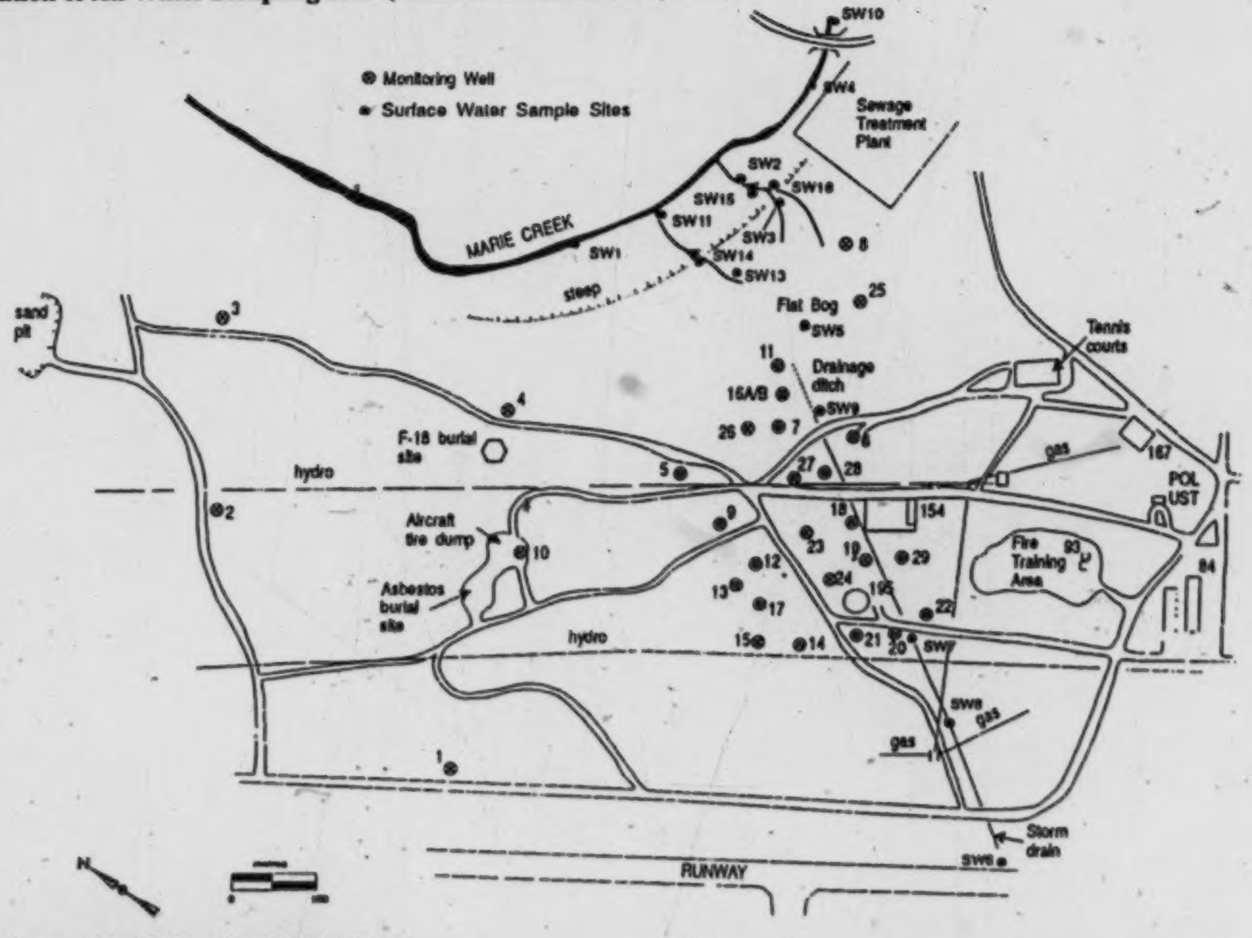
Map compiled from Site Record Dwg. L-C252-8429, updated from aerial photo A27209-214 and field observations.


Drainage to Marie Creek
1745
1750
1755
1760
1765
1770
25
16A/B
26
28
27
Dry Storage
18
23
12
19
29
Gas Pipeline
13
24
17
195
32
34
30
31
22
15
33
14
21
20
36
35
N
metres
0
50
Legend
Manhole
Drainage ditch
195
Sand Storage Building
Borehole with no well
Well location and number
Gravel roads
Overhead Hydro lines
Storm sewer line from runway

Map compiled from Site Record Dwg. L-C252-8429, updated from aerial photo A27208-214 and field observations.

Figure 4-4: Location of New RRMC Boreholes (Modified From RRMC, 1991)

Figure 4-5: Location of All Water Sampling Sites (Modified From RRMC, 1991)


● Monitoring Well
● Surface Water Sample Sites
MARIE CREEK
SW1
SW2
SW3
SW4
SW5
SW6
SW7
SW8
SW9
SW10
SW11
SW13
SW14
SW15
SW16
Sewage Treatment Plant
steep
sand pit
Flat Bog
Drainage ditch
Tennis courts
F-18 burial site
Aircraft tire dump
Asbestos burial site
Fire Training Area
POL UST
hydro
hydro
gas
gas
gas
Storm drain
RUNWAY
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16A/B
17
18
19
20
21
22
23
24
25
26
27
28
29
154
167
195
93
84
N
0

Map compiled from Site Record Dwg. L-C252-8429, updated from aerial photo A27209-214 and field observations.

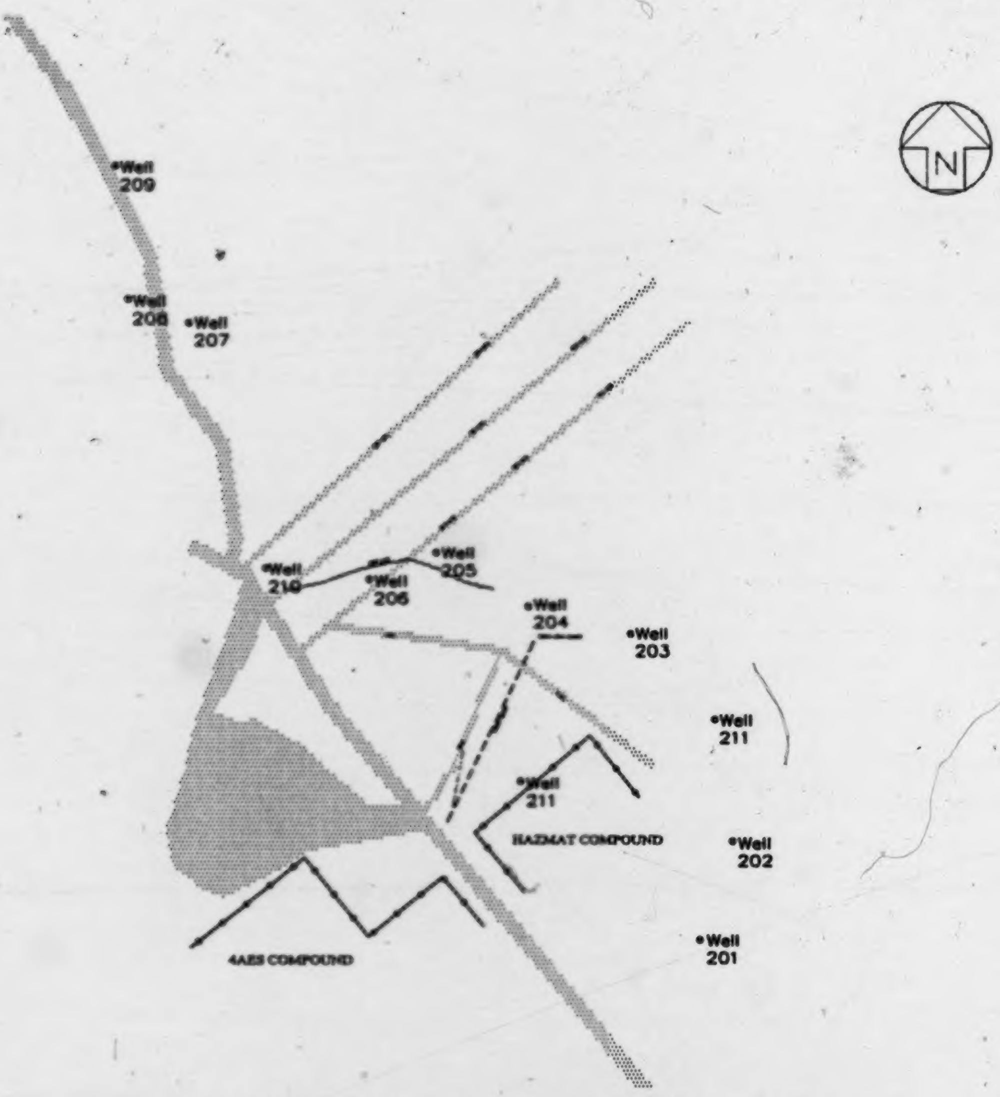

N
Well 209
Well 208
Well 207
Well 210
Well 206
Well 205
Well 204
Well 203
Well 211
Well 211
HAZMAT COMPOUND
Well 202
Well 201
4AES COMPOUND

Figure 4-6: Wells Installed By An-Geo (Modified From An-Geo, 1997)

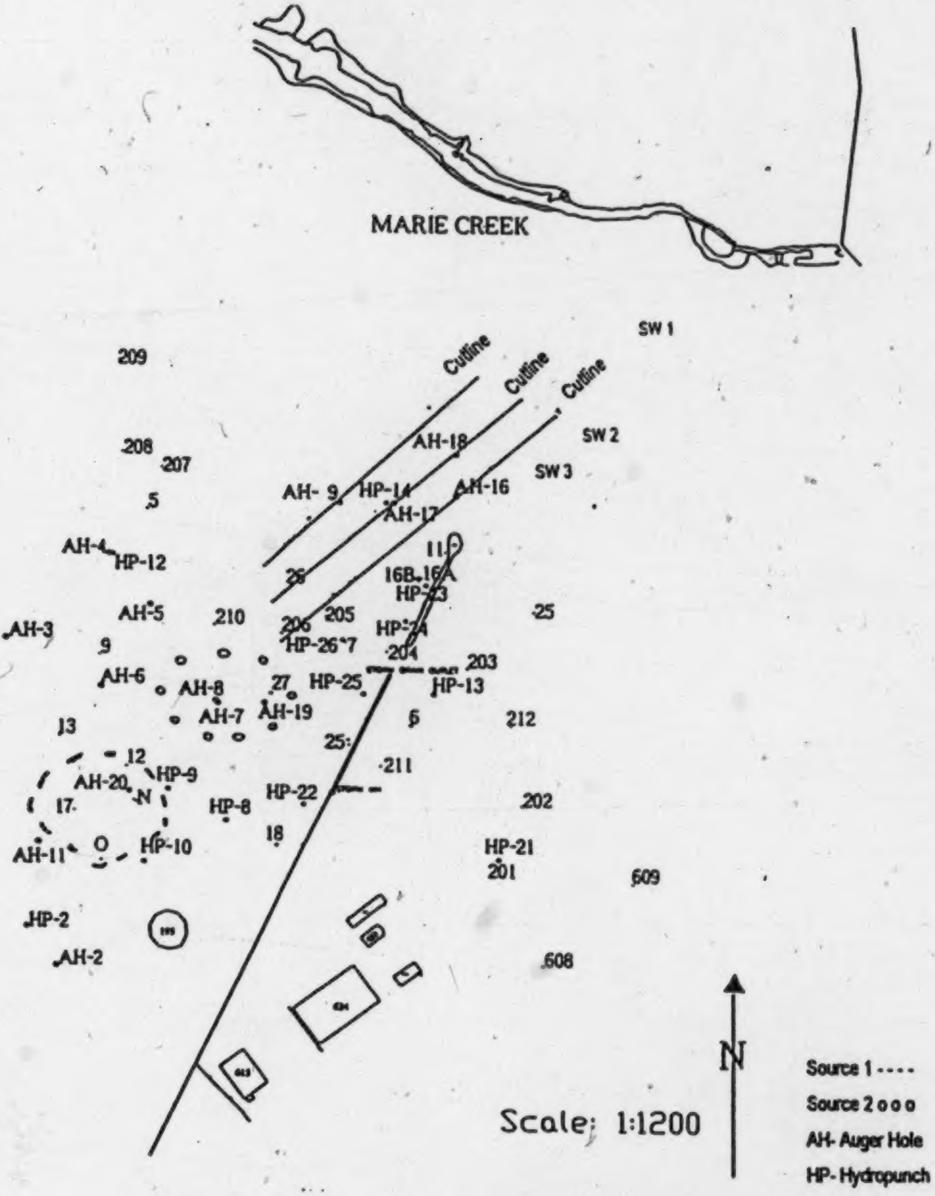
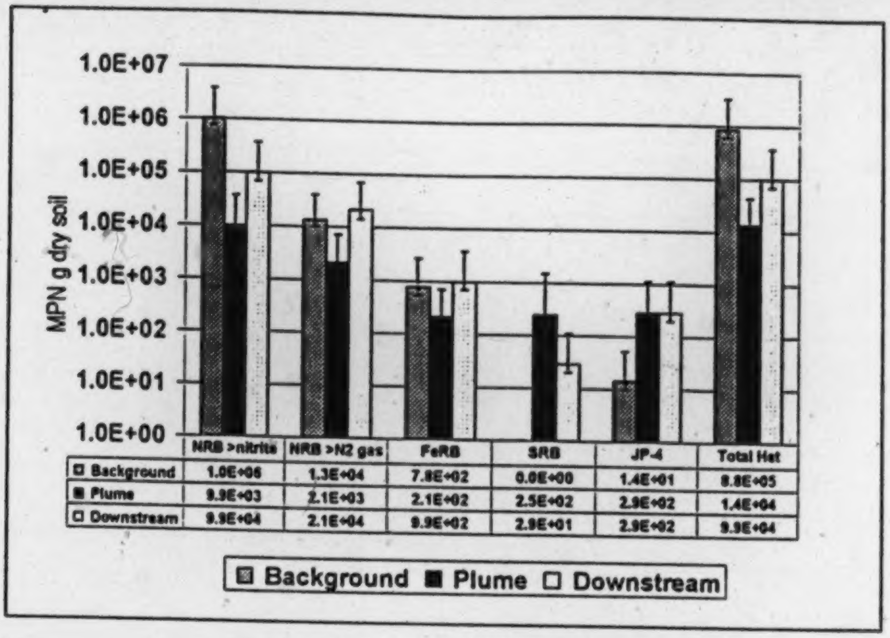

MARIE CREEK
SW 1
209
Cutline
Cutline
Cutline
AH-18
SW 2
208
207
SW 3
AH- 9
HP-14
AH-16
5
AH-17
AH-4
HP-12
11
26
16B
16A
HP-23
AH-5
210
206
205
HP-24
25
AH-3
HP-26
7
204
9
203
AH-6
AH-8
27
HP-25
HP-13
AH-7
AH-19
6
212
13
25
12
211
AH-20
HP-9
N
17
HP-8
HP-22
202
18
HP-21
AH-11
O
HP-10
201
609
HP-2
AH-2
608
N
Scale: 1:1200
Source 1 - - - -
Source 2 o o o
AH- Auger Hole
HP- Hydropunch

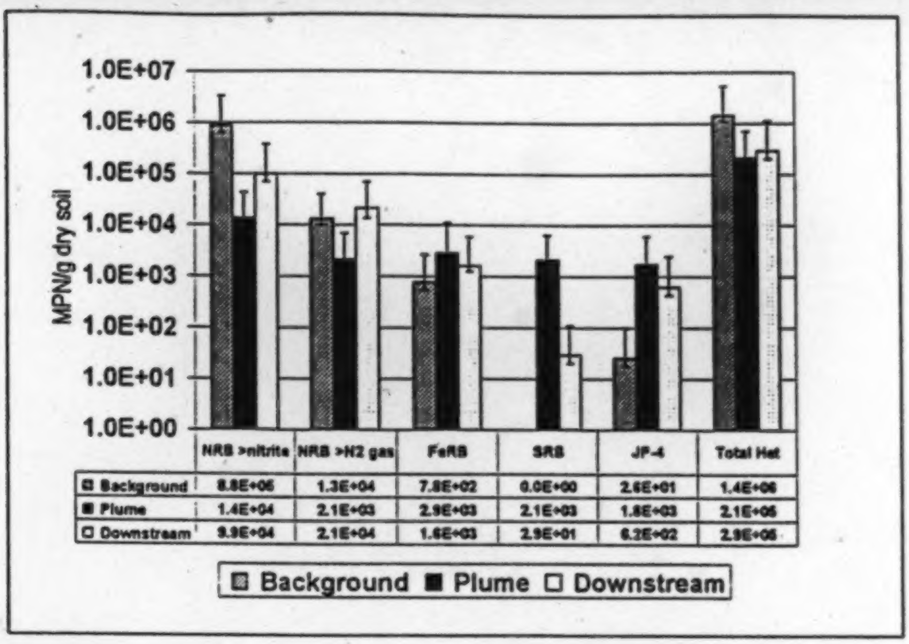
Figure 4-7: University of Alberta Sampling Locations (Mullick, 1999)



	NRB >nitrite	NRB >N2 gas	FeRB	SRB	JP-4	Total Het
▨ Background	1.0E+06	1.3E+04	7.8E+02	0.0E+00	1.4E+01	8.8E+05
■ Plume	9.9E+03	2.1E+03	2.1E+02	2.5E+02	2.9E+02	1.4E+04
☐ Downstream	9.9E+04	2.1E+04	9.9E+02	2.9E+01	2.9E+02	9.9E+04

NRB > Nitrite: nitrate reducing bacteria that produce nitrite
FeRB: iron-reducing bacteria
JP-4: JP-4 degrading bacteria
NRB > N_2 gas: nitrate reducing bacteria that produce N_2 gas
SRB: sulfate-reducing bacteria
Total Het: total heterotrophic bacteria

Figure 4-8: MPN Results - After 4 Weeks Incubation at 22°C (Mullick, 1999)



	NRB >nitrite	NRB >N2 gas	FeRB	SRB	JP-4	Total Het
▨ Background	8.8E+05	1.3E+04	7.8E+02	0.0E+00	2.6E+01	1.4E+06
■ Plume	1.4E+04	2.1E+03	2.9E+03	2.1E+03	1.8E+03	2.1E+05
☐ Downstream	9.9E+04	2.1E+04	1.6E+03	2.9E+01	6.2E+02	2.9E+05

NRB > Nitrite: nitrate reducing bacteria that produce nitrite
FeRB: iron-reducing bacteria
JP-4: JP-4 degrading bacteria

NRB > N_2 gas: nitrate reducing bacteria that produce N_2 gas
SRB: sulfate-reducing bacteria
Total Het: total heterotrophic bacteria

Figure 4-9: MPN Results - After Additional 2 Weeks Incubation at 22°C (Mullick, 1999)

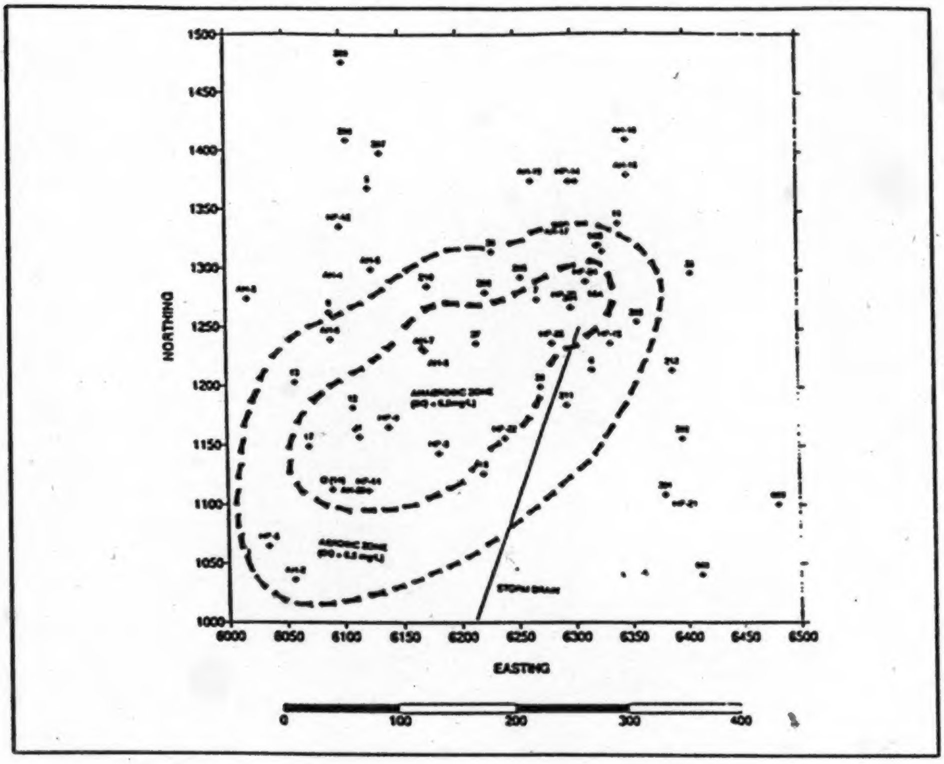

1500
1450
1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
6500
EASTING
ANAEROBIC ZONE
AEROBIC ZONE
STORM DRAIN
0
100
200
300
400

Figure 4-10: Interpretative Aerobic and Anaerobic Zones (Mullick, 1999)

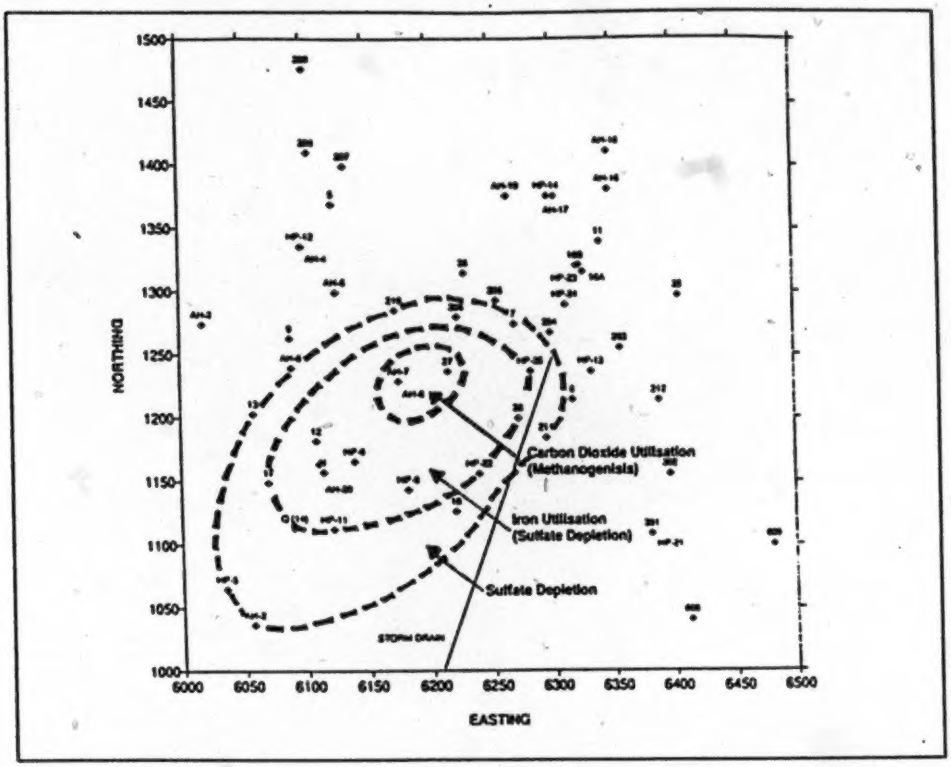

NORTHING
EASTING
1500
1450
1400
1350
1300
1250
1200
1150
1100
1050
1000
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
6500
AH-2
HP-12
AH-6
AH-7
27
13
12
HP-4
AH-20
HP-11
HP-13
21
11
16A
Carbon Dioxide Utilisation
(Methanogenisis)
Iron Utilisation
(Sulfate Depletion)
Sulfate Depletion
STORM DRAIN

Figure 4-11: Interpretative Zones of Electron Acceptor Utilization (Modified From Mullick, 1999)

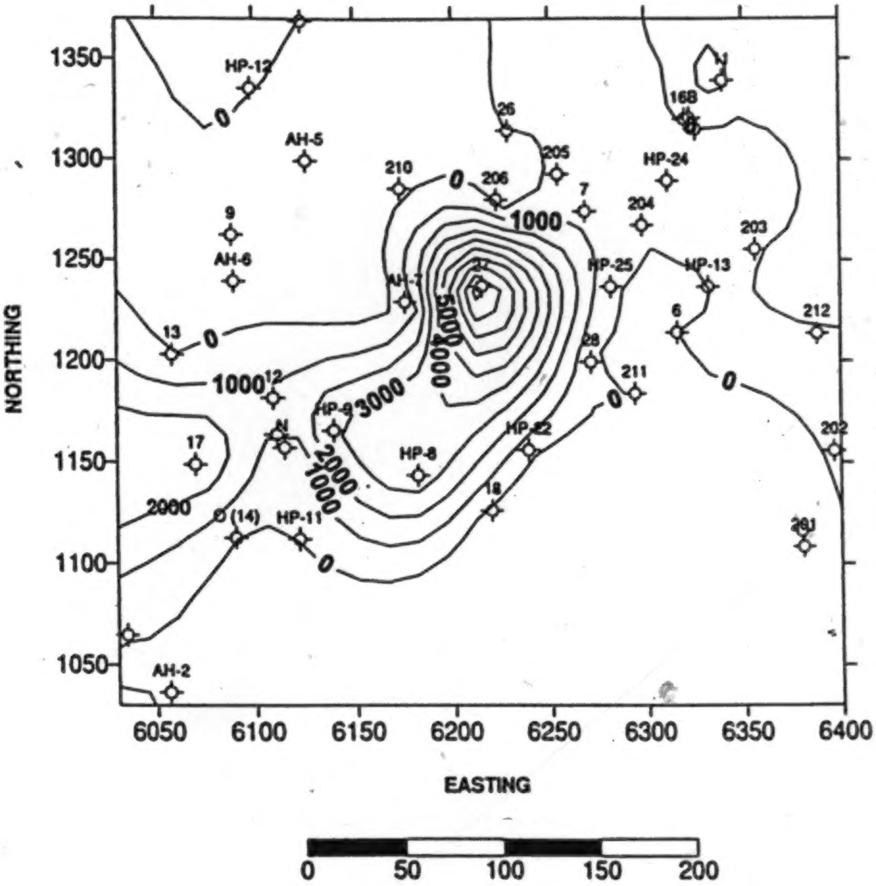

HP-12
AH-5
210
0
206
26
205
HP-24
16B
7
204
1000
9
AH-6
203
AH-7
27
5000
4000
HP-25
HP-13
212
6
13
0
28
1000
12
3000
211
0
HP-9
N
HP-22
202
17
HP-8
2000
1000
2000
18
O (14)
HP-11
0
AH-2
1350
1300
1250
1200
1150
1100
1050
NORTHING
6050
6100
6150
6200
6250
6300
6350
6400
EASTING
0
50
100
150
200

Figure 4-12: Interpretative Groundwater Isopleth of 1,1,1-Trichloroethane (ppb) (Mullick, 1999)

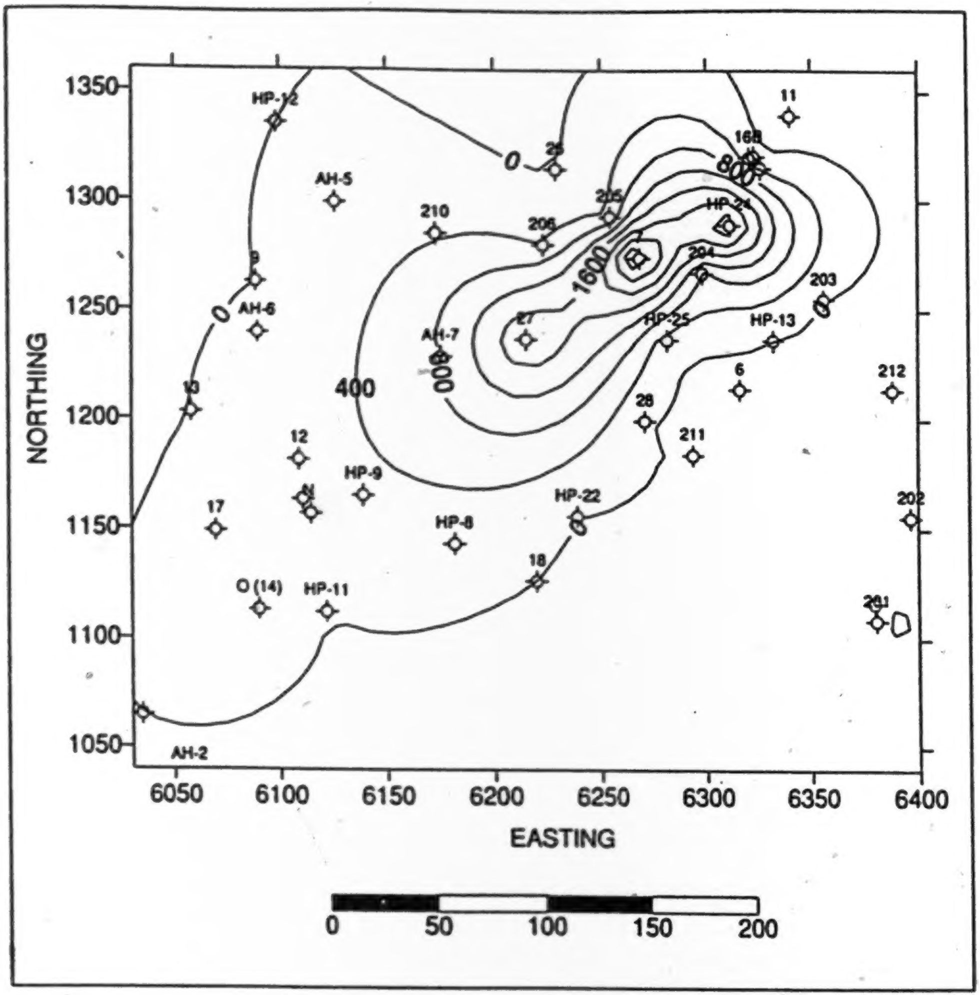

1350
1300
1250
1200
1150
1100
1050
NORTHING
6050
6100
6150
6200
6250
6300
6350
6400
EASTING
HP-12
AH-5
210
206
205
25
0
11
168
800
HP-24
1600
204
203
9
0
AH-6
27
AH-7
800
HP-25
HP-13
0
13
400
6
212
28
211
12
HP-9
N
17
HP-22
202
HP-8
18
O (14)
HP-11
201
AH-2
0
50
100
150
200

Figure 4-13: Interpretative Groundwater Isopleth of 1,1-Dichloroethane (ppb) (Mullick, 1999)

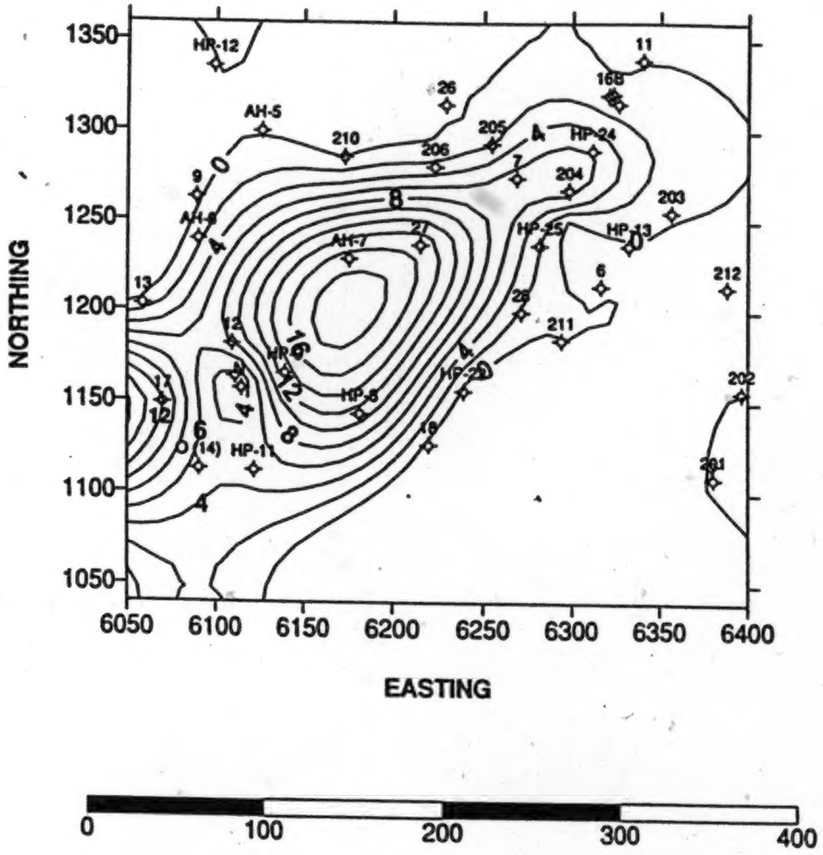

NORTHING
EASTING
1350
1300
1250
1200
1150
1100
1050
6050
6100
6150
6200
6250
6300
6350
6400
HP-12
AH-5
210
26
206
205
HP-24
168
11
9
AH-6
7
204
203
27
AH-7
HP-25
HP-13
13
6
212
12
HP-9
28
211
17
HP-8
HP-23
202
(14)
HP-11
18
201
0
4
8
12
16
6
0
100
200
300
400

Figure 4-14: Interpretative Groundwater Isopleth of BTEX (ppm) (Mullick, 1999)

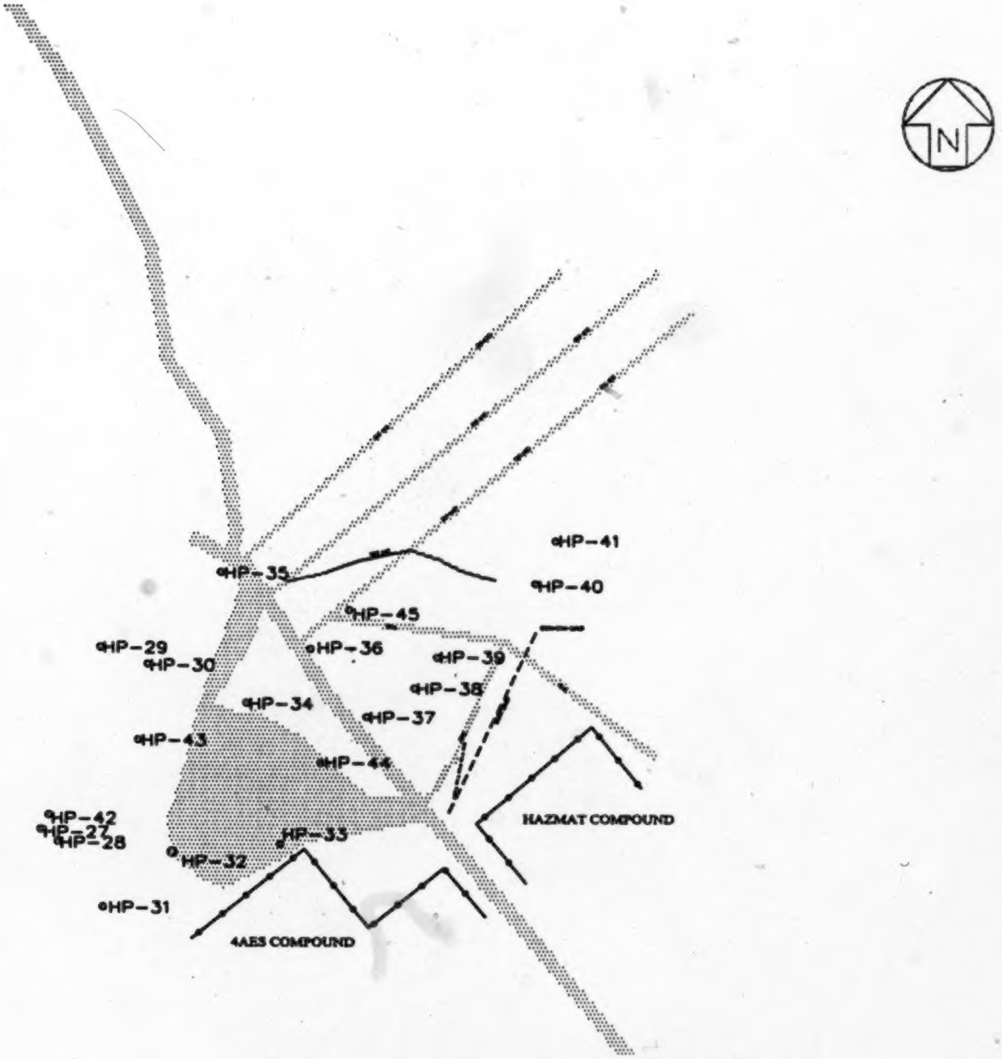

N
HP-41
HP-35
HP-40
HP-45
HP-29
HP-36
HP-30
HP-39
HP-38
HP-34
HP-37
HP-43
HP-44
HP-42
HP-27
HP-28
HP-33
HAZMAT COMPOUND
HP-32
HP-31
4AES COMPOUND

Figure 4-15: Sampling Locations, November, 1999

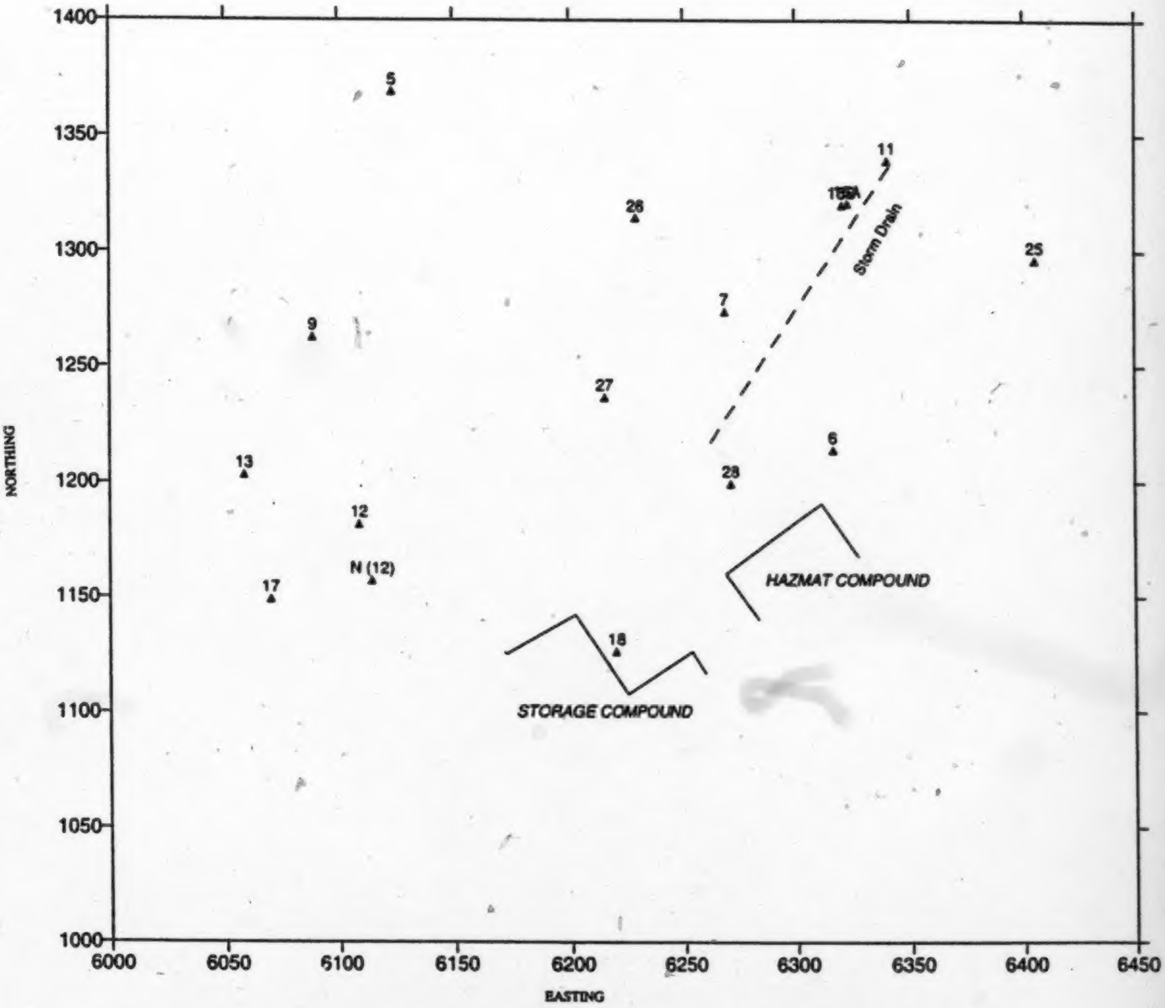


Figure 4-16: 1991 Sampling Points (Modified From RRMC, 1991)

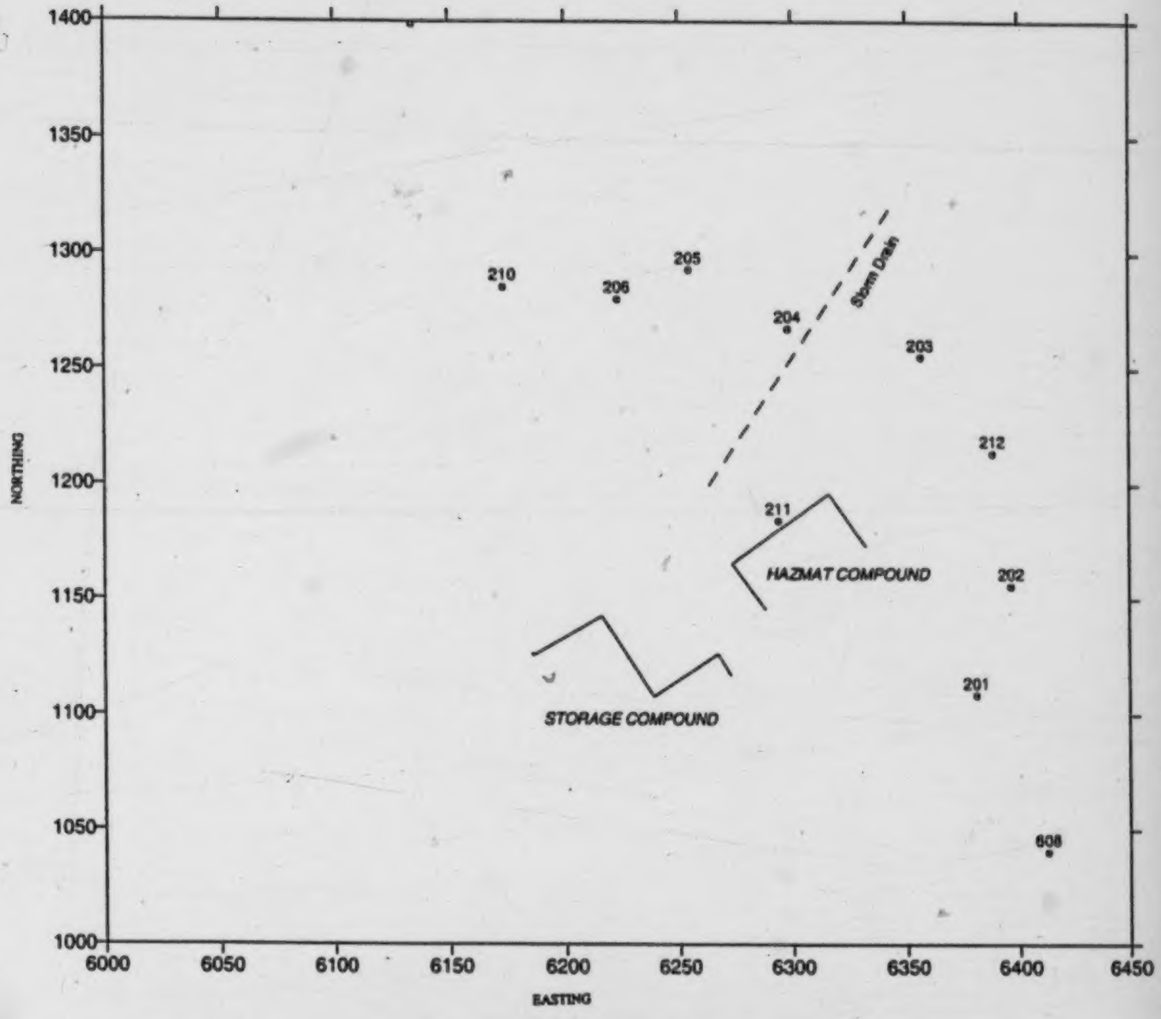

1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING
210
206
205
204
203
212
211
202
201
608
Storm Drain
HAZMAT COMPOUND
STORAGE COMPOUND

Figure 4-17: An-Geo Sampling Points (Modified From An-Geo, 1997)

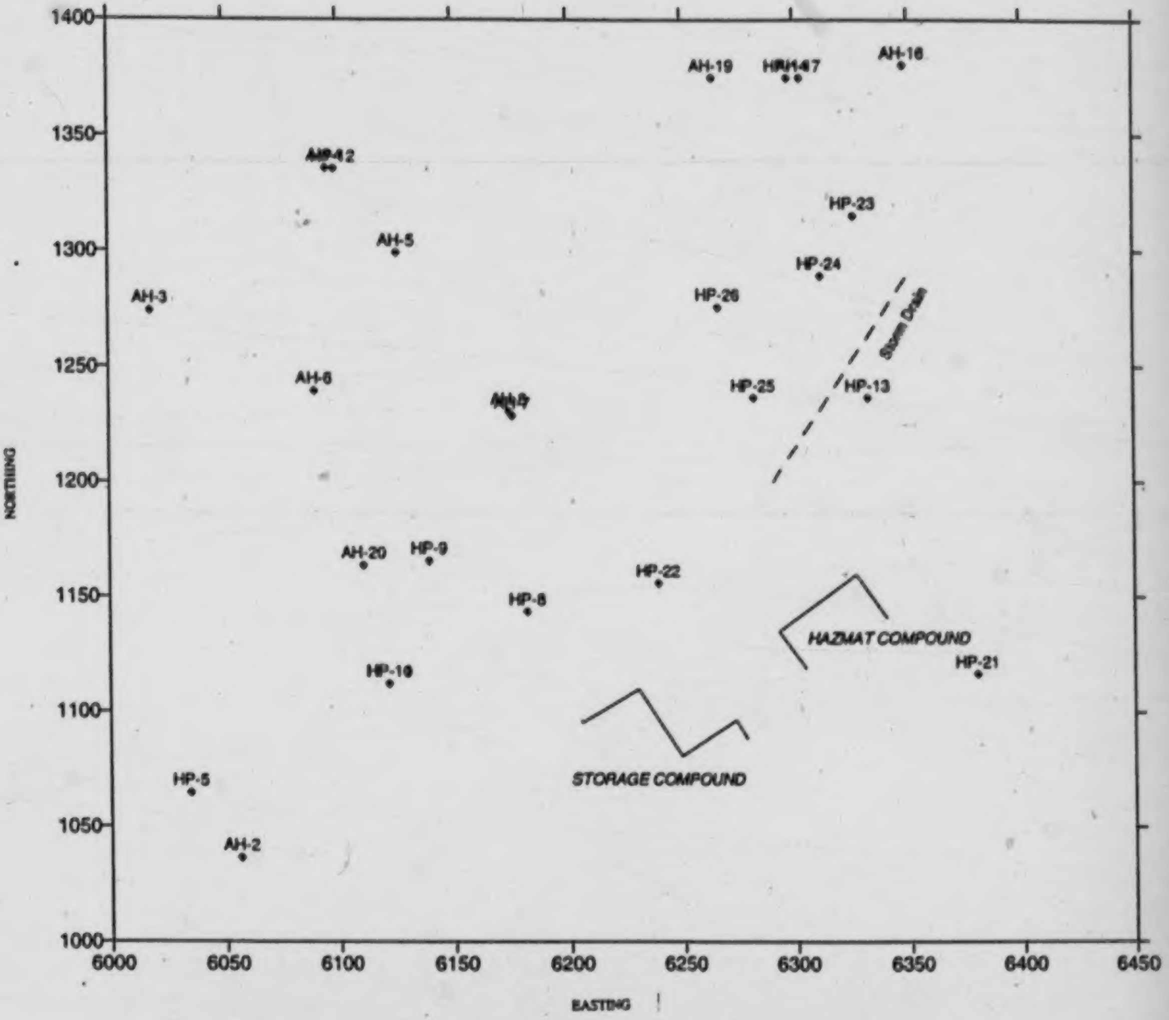


Figure 4-18: 1998 Sampling Points (Modified From Mullick, 1999)

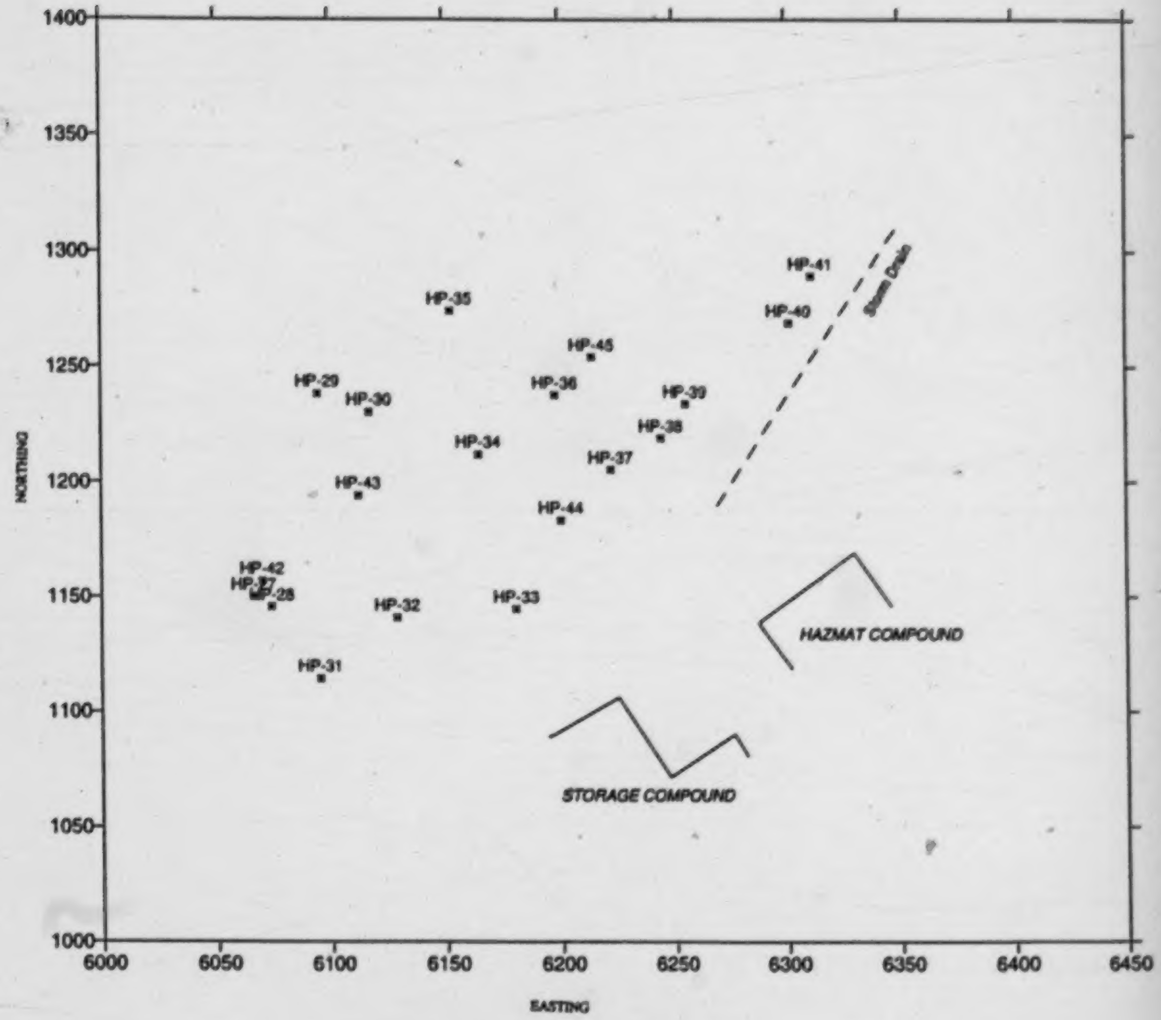


Figure 4-19: 1999 Sampling Points

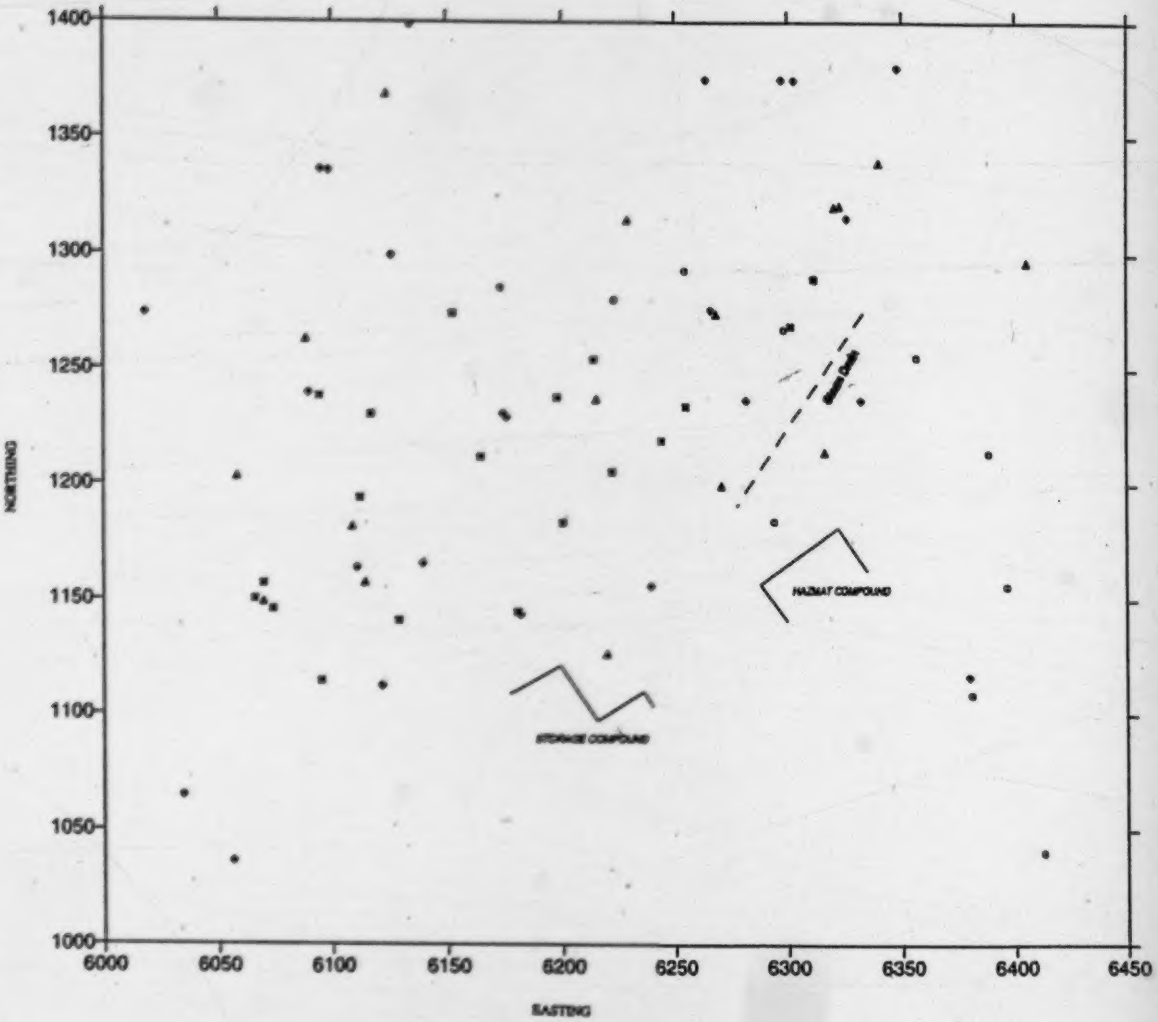


Figure 4-20: All Sampling Points

Figure 4-21: Drill Rig and Teflon Tube for Hydropunch® Sampling

Figure 4-22: Flow-Through Cell for Groundwater Parameter Measurement

Figure 4-23: Solid Stem Auger for Collection of Soil Samples

5.0 RESULTS

5.1 CALCULATIONS

5.1.1 Groundwater Velocity Calculations

Table 5-1 shows the groundwater elevations that were gathered from 1998 to 1999. The groundwater elevations for the July 1999 measurements are shown in a contour plot in Figure 5-1. The groundwater elevation was approximately 537 m upstream of the site and approximately 533 m at the downstream edge. The measured elevations differed from the 1998 values by 0.2 m to about 1 m maximum.

The hydraulic gradient is calculated from

$$i = \frac{\Delta H}{\Delta L} \qquad [11]$$

where ΔH is the difference between two heads, and ΔL is the distance between the two points of different head. The two points of different head were assumed to be perpendicular to the groundwater contours.

The hydraulic gradient was approximately 1.1×10^{-2}. This compares to 1.1×10^{-2} from the Mullick (1999) study. The groundwater seepage velocity, v_x, is calculated from Darcy's Law:

$$v_x = \frac{-K}{n_e}\frac{\Delta H}{\Delta L} \qquad [12]$$

where v_x = average linear groundwater velocity parallel to groundwater flow direction (seepage velocity) (m/yr)

K = hydraulic conductivity (m/s)

n_e = effective porosity (unitless)

$\Delta H/\Delta L$ = hydraulic gradient (unitless)

For K = 7.5 x 10^{-5} m/s (Mullick, 1999), n_e = 0.31 (calculated in Appendix D) and i = 1.1 x 10^{-2} then v_x= 84 m/yr. This value of seepage velocity and the 76 m/yr from the Mullick study are virtually identical. Table 5-2 provides limits in the minimum, maximum and expected values of k, i, and v_x.

The retarded contaminant transport velocity, v_c, is calculated from:

$$V_C(m/yr) = \frac{V_x}{R} \qquad [13]$$

where v_x = seepage velocity (m/yr)

and R = coefficient of retardation (dimensionless)

The calculation of the retardation coefficient for this site is contained in Appendix D. The value obtained for TCA was 2.0, indicating that approximately one-half of the contaminant is present in the aqueous phase and one-half is sorbed onto the particles in the aquifer. CAHs do not tend to sorb to soils and aquifer materials as readily as do many other hazardous chemicals. Nevertheless, sorption in aquifer systems is sufficient to retard that rate at which they move in ground water in relation to the movement of ground water itself (McCarty and Semprini, 1994). Thus, the retarded TCA transport velocity was estimated to be approximately 40 m/yr. Table 5-3 shows the minimum, maximum and expected contaminant velocities with changes in seepage velocity. The contaminant velocities were calculated using the calculation procedure outlined in

Appendix D, and the minimum and maximum ranges shown in Table 5-3 were calculated based on the varying seepage velocity.

5.1.2 First Order Rate Constants for Biological Decay

Weidemeier et al. (1999) suggested a method to calculate the biodegradation rate that was derived by Buscheck and Alcantar (1995) based on measured concentration data at a field site. The Buscheck and Alcantar (1995) equation involves interpretation of data from a steady-state contaminant plume and is based on the one-dimensional steady-state analytical solution to the advection-dispersion equation presented by Bear (1979). The equation is as follows:

$$\lambda \cong \frac{v_c}{4\alpha_x}\left(\left[1+2\alpha_x\left(\frac{k}{v_x}\right)\right]^2-1\right) \qquad [14]$$

where λ = first order biodegradation rate constant

v_c = retarded contaminant velocity in the direction of groundwater flow

α_x = longitudinal dispersivity

k/v_x = slope of the line formed by plotting the logarithm of the contaminant concentration versus distance downgradient along the flow path, and is found by linear regression.

In Equation [14], it is assumed that the contaminant plume has reached steady-state.

Calculations of rates of degradation for TCA and DCA degradation by the Buscheck and Alcantar (1995) method are shown in Figures 5-2 and 5-3. The degradation rates were found to be 7.69 yr^{-1} for TCA degradation and 0.29 yr^{-1} for anaerobic DCA degradation.

These rates translate to half lives of 0.09 yr and 2.3 yr for TCA and DCA, respectively. The TCA half life appears to fit in with the literature reported rates. The DCA half life, however, is slightly higher than the range of 0.32 to 1.7 years, reported by Howard et al. (1991). The sensitivity analysis is shown in Table 5-4. The calculation shows that the degradation rate is slightly more sensitive to changes in dispersivity than changes in seepage velocity. The calculated degradation is also very sensitive to the k/v_x. Comparison to values obtained from the literature indicates that the value for DCA using Equation 11 appears reasonable but that of TCA is somewhat higher than it should be.

5.2 RESULTS OF FIELD SAMPLING

5.2.1 Groundwater Geochemistry

Table 5-5 shows the results of the groundwater geochemical analyses. The pH of the groundwater across the site ranged from 6.0 to 6.9, indicating neutral conditions for microbial growth and optimal pH for degradation of CAHs, which is between 6 and 8 (Lee et al., 1998).

The EC showed a wide range across the site, from 109 µS/cm at Well 210 to 61610 µS/cm, at HP-36. HP-36 is directly downstream from building 195, which had stored salt for road deicing that has presumably leached into the groundwater. It is possible, in some instances, that the presence of chloride above background conditions can be used as an indication of reductive dechlorination. However, at this site, the conductivity data could not be used as such an indicator for reductive dechlorination since there was a nearby building that was probably leaching salt and it was interfering with the chloride concentrations.

The initial redox potential results were incorrect because the probe was malfunctioning. New redox potential values were taken for Well 27 and Well N in July, 2000, and the values found were -346mV and –16mV, respectively. These values indicate reducing conditions at the site, which is typical of contaminated sites where intrinsic biodegradation is ongoing (Chapelle et al., 1996).

5.2.2 Terminal Electron Acceptor Conditions

Table 5-5 also shows the measured DO values from the November 1999 groundwater sampling event. Some of the measured DO values were quite high, and it is believed that the DO meter was either improperly calibrated or that the probe membrane was not functioning. The DO values were measured at values > 3 mg/L where the redox potential values indicated reducing conditions and methane was detected. New downhole DO measurements were taken in July, 2000, for Well 27 and Well N and these values were:

Well	DO (mg/L)
27	1.70
N	1.13

Additional downhole DO values were taken again in August, 2000, and they were found to be:

Well	DO (mg/L)
17	1.34
N	1.21
27	1.50
206	1.90
204	1.08

These DO values were all above 1 mg/L, which conflicts with some of the anaerobic indicators. It is possible that diffusion of oxygen into the well water may account for these low but measurable values. The DO values measured in the Hydropunch® samples were believed to be unreliable since these samples were likely somewhat aerated during sampling using the small diameter Waterra™ pump.

Table 4-9 shows the electron acceptor and microbial byproduct concentrations found at the site in November, 1999. Figure5-4 shows the perceived anaerobic and aerobic zones across the site. Low DO values correspond with the anaerobic zone and the higher DO values correspond with the background areas outside of the plume.

Nitrates and nitrites, across the site and upgradient, ranged from 0.1 to 0.5 mg/L, all close to non-detect, with two inexplicably high values at 2.4 and 20.7 mg/L at Well 211 and Well 13. These values conflict with previous measurements and trends across the site, and so are believed to be erroneous. It is also possible that the high values result from a source in the landfill. It is likely that nitrate reduction plays an insignificant role in degradation of the contaminants since there is insufficient nitrate.

The reduction of sulfate concentrations in the zone of contamination indicates sulfate reduction may be occurring; however, trends continue to be elusive, as there is considerable scatter in the data spatially. It is possible that sulfate has entered the groundwater from the land-fill giving the higher measured values within the plume and causing the inconsistency in the values. Hence the magnitude of sulfate reduction is uncertain.

Figure 5-5 shows the iron (II) distribution across the site. The reduction of iron (III) to iron (II) is believed to be unable to proceed without microbial mediation (Lovley, 1997). Therefore, the presence of iron (II) strongly suggests that iron (III) is being used as an electron acceptor at the site. The iron (II) concentrations in the groundwater increased from non-detect at the periphery of the plume to more than 200 mg/L in the plume core. Furthermore, based on the measurements of iron (II) from Mullick (1999), iron (II) was present as far downgradient as HP-23, Well 16, and possibly HP-14. This data imply that iron reduction may be a very significant component of the biodegradation capacity.

Methane values in Table 4-9 show that concentrations close to the center of the plume were greater than 0.5 mg/L. Figure 5-6 shows the methane distribution. The anaerobic zone was determined to be within the centre of the plume between Well 17 and HP-41. An aerobic zone surrounded this anaerobic core, as shown in Figure 5-4. These results correlate well with the elevated methane concentrations found in the same areas (Figure 5-6). Methane background concentrations were non-detectable, whereas towards the plume centre the concentrations were greater than 1.0 mg/L. Small amounts of methane were observed at HP-40 and 41, and significant amounts were observed at Well 206. According to the Weidemeier et al. (1999) scoring system, methane values greater than 0.5 mg/L indicate in-situ conditions suitable for reductive dechlorination. Therefore, measurable concentrations of methane across most of the plume indicate that the zone is highly reduced and will favor reductive dechlorination.

Given the above, iron reduction and methanogenesis appear to be the predominant electron accepting processes, with the possibility of some sulfate reduction. The core of the contaminant plume is thus anaerobic and moderately to highly reduced. These conditions favor reductive dechlorination as an electron accepting process. There is some scatter in the results, which is believed to result from local heterogeneities in hydrogeologic conditions and total electron acceptor conditions. Nonetheless, the overall trends described are quite strongly supported by the data.

5.2.3 Weidemeier et al. (1999) Scoring System

According to Weidemeier et al. (1999), as discussed previously in section 2.7, the site can be given a score based on the presence of conditions conducive for reductive dechlorination.

The scores obtained for the site were:

Concentration in most contaminated zone	Score
DO > 1 mg/L	-3
Nitrate < 1 mg/L	2
Fe (II) > 1 mg/L	3
Sulfate < 20 mg/L	2
Methane > 0.5 mg/L	3
ORP (oxygen reduction potential) ORP < -100 mV	2
5< pH < 9	0
TOC > 20 mg/L	2
BTEX > 0.1 mg/L	2
1,1-dichloroethane	2

The total score is for the site is 15. A score between 15 and 20 indicates that there is adequate evidence for anaerobic biodegradation of chlorinated organics (Weidemeier et al., 1999).

5.3 LABORATORY TESTING RESULTS

5.3.1 Results of The Microcosm Tests

The procedure of the microcosm tests were described in Chapter 4.2.2.2 and the results are discussed below. Figures 5-7a, 5-7b, 5-8a, and 5-8b show the concentration versus time graphs for samples taken from Well 27 at the two temperatures, 20°C and 10°C. Each figure shows two plots. The first plot shows average values for triplicate, destructive 30 mL test vials, with the error bars representing one standard deviation for the sampling event. The second plot, underneath the first plot contains error bars representing minimum, maximum, and mean concentrations for the sampling event. At 20°C, the average starting concentration of TCA (October 20, 2000) was approximately 12 480 µg/L. By December, two months later, the concentration had decreased to an average of 11 850 µg/L. The measured concentration then appeared to increase and peaked at 17 610 µg/L in the end of December, 2000, decreased to 9866 µg/L by 9 January, and then reached an average of approximately 8890 µg/L by 10 March. The data appear to show approximately a 21% decrease in TCA from the first four sampling events to the last six sampling events. The last sampling event on March 20, 2001, however, showed a sharp increase, to approximately 12 370 µg/L, close to the original starting concentration. The data was highly variable, as indicated by the higher than expected concentrations for TCA found from the three sampling events taken from December 18 to January 8, 2001, and large scatter within the triplicate samples. Furthermore, the concentrations measured from the microcosm samples were greater than the expected 9700 mg/L because the dilution of the groundwater (50% groundwater and 50% distilled water) caused more contamination to transfer from the soil to the groundwater. The mass balance to determine the exact amount transferred could not be done.

The concentrations for DCA (Figures 5-7b and 5-8b) were approximately 1360 μg/L at time 0 and fluctuated between 1200 μg/L and 2000 μg/L over the test duration. Although an increase in DCA concentration was anticipated, given the scatter in the test results an increase was not apparent. The 1,3 and 1,4-DCBs were non-detectable in the samples.

At 10°C (Figure 5-8a), the average concentration of TCA for time 0 was approximately 11 950 μg/L. The concentrations peaked at approximately 18 730 μg/L on December 20, and then decreased again to an average of approximately 11 740 μg/L for the last four sampling events. Again, the large scatter in the data showed that there was uncertainty in what the true value of concentration should be.

The DCA concentrations at 10°C (Figure 5-8b) started at 1460 μg/L and fluctuated between a range of 1300 μg/L to 2100 μg/L. At the end of the experiment the values were approximately 1700 μg/L, showing a slight increase from the starting values. However, the large scatter in the data once again showed uncertainty of an increase in concentration. The 1,3 and 1,4-DCBs were all non-detectable.

Figures 5-9a, 5-9b, 5-10a, and 5-10b show the concentration versus time graphs for all compounds at Well N for the two temperatures (20°C and 10°C). For Well N, at 20°C, the concentration of TCA at time 0 was 12 180 µg/L, but the average concentration fluctuated throughout the sampling events, ranging from 12 180 µg/L to approximately 39 220 µg/L, almost three times higher than the original values.

The DCA concentrations (Figure 5-9b) averaged approximately 640 µg/L over all the sampling events, ranging from 390 µg/L to 850 µg/L. There was, however, a discernable increase in DCA over the duration of the experiment; there was a 60% increase from approximately 500 µg/L at the start to approximately 800 µg/L at the end.

At 10°C, the starting concentrations for TCA (Figure 5-10a) were an average of approximately 11 560 µg/L. Like the values at the higher temperature, the concentration fluctuated throughout the sampling events, with even larger ranges from 11 560 µg/L to 63 400 µg/L, almost six times larger than the initial values.

The DCA concentrations (Figure 5-10b) averaged approximately 720 µg/L over all the sampling events, with a range from 530 to 940 µg/L. There appears to be an approximately 33% increase in DCA from the start of the experiment to the end, increasing from approximately 550 µg/L to approximately 800 µg/L. The 1,3 and 1,4-DCBs were all non-detectable.

Figures 5-11 and 5-12 are the graphs for negative controls for Well 27 at both temperatures (10°C and 20°C) that contained both soil and ground water, to quantify the change in contaminant concentration in groundwater due to processes other than biodegradation (sorption, volatilization, or abiotic chemical reactions). The concentration of TCA at Well 27 at 20°C was very high in the first sampling event, immediately after the negatives were spiked. However, following the first sampling event, TCA concentrations averaged at approximately 10 440 µg/L ± 5000 µg/L and showed considerable scatter. DCA values averaged 2820 µg/L ± 1500 µg/L, also considerably scattered. At 10°C (Figure 5-12), the average concentrations of TCA at Well 27 were 7820 µg/L and values were relatively steady around that value after the first sampling event. DCA concentrations were relatively steady at approximately 1960 µg/L.

At Well N for 20°C (Figure 5-13), it was anticipated that the values for TCA and DCA would be approximately 1900 µg/L and approximately 660 µg/L, respectively (these were the spiked concentrations). The concentrations for TCA in the sampling events were considerably scattered, ranging from approximately 900 µg/L to 5000 µg/L. However, the DCA values averaged at approximately 508 µg/L ± 100 µg/L, which were close to the expected values. At 10°C (Figure 5-14), the steady average of the TCA concentrations after the second sampling event, was 842 µg/L and DCA values fluctuated from 320 µg/L to 570 µg/L. Some high concentrations of both 1,4-DCB and 1,2-DCB were found in the first sampling event. These outlying DCB values are discussed in Chapter 6.

Figures 5-15a and 5-15b show the graphs for negative controls at Well 27 that contained only ground water (for both temperatures). Examination of these negative controls shows, at 20°C, the concentrations of TCA (Figure 5-15a) at Well 27 fluctuated and the average value excluding the first value was 13 800±1250 µg/L and the DCA values averaged very steadily at approximately 2780 µg/L.

At 10°C (Figure 5-15b), the TCA concentrations at Well 27 were fluctuating and averaged approximately 10 780±3500 μg/L, excluding the first value. The DCA values, however, were very steady, and were approximately 2370 μg/L.

At Well N (Figures 5-16a and 5-16b), the average concentration of TCA was relatively steady at approximately 1020±250 μg/L. DCA values averaged at approximately 600±100 μg/L. The 1,3-DCB values were higher than the TCA values in the first sampling event and reached up to 900 μg/L in the last three. 1,2-DCB concentrations increased from approximately 400 μg/L to approximately 1200 μg/L in the last three sampling events.

At 10°C (Figure 5-16b), the TCA concentrations were steady at approximately 940±100 μg/L and the DCA concentrations were steady at approximately 510±50 μg/L.

Table 5-1: Groundwater Elevations From June 1998 to July 1999

				June 15,1998	Aug 6,1998	Oct 27,1998	June 4, 1999	July 22, 1999
Hole I.D.	Northing (m)	Easting (m)	Ground elevation (m)	Water Elev. (m)	Water Elev. (m)	Water Elev. (m)	Water Elev. (m)	Water Elev. (m)
4	1590.103	6035.867	536.6	535.1	534.2		534.1	534.0
5	1368.835	6124.015	535.1	533.0				533.6
6	1214.115	6316.219		535.2	535.4	535.3	535.3	535.2
7	1274.128	6268.621	536.8	534.8	535.0	534.9		534.8
9	1262.791	6088.838	537.4		536.4	536.0	536.4	536.0
12	1181.719	6109.189	538.7	536.6		536.5	536.7	536.5
13	1203.204	6058.503	538.4	536.8	536.8	536.6	537.0	536.6
16B	1320.174	6320.68	534.9		533.7	532.9	533.8	533.5
17	1149.058	6069.809	538.9	537.2		537.0	537.3	537.0
18	1126.272	6219.62	538.7	536.2	536.6			536.2
25	1296.559	6405.136	534.1			533.7	533.1	533.6
26	1314.492	6228.896	536.1	535.1	535.3	535.1	535.3	535.0
27	1236.719	6214.966	538.0	535.6	535.9	535.6	535.8	535.7
28	1199.504	6271.26	537.8	535.6	535.9		535.7	535.6
201	1108.526	6380.479	539.3	539.7	536.4	536.3	536.4	536.3
202	1155.715	6396.444	539.2	536.0	536.3	536.1	536.2	536.0
203	1255.284	6356.322	535.7		535.0	535.0	535.0	534.8
204	1267.334	6298.29	536.4		534.8	534.8	534.8	534.7
205	1292.868	6254.553	536.4	535.0	535.1	534.0	534.8	534.9
206	1280.019	6222.76	536.8	535.8	535.6	535.4	535.6	535.3
207	1398.872	6134.271	535.2	533.7	533.8	533.5	533.9	533.5
208	1409.679	6105.216	535.3	533.8	533.8	533.6	534.0	533.6
209	1476.137	6102.449	535.1	533.3	533.3		533.7	533.1
210	1285.313	6173.267	536.8		536.0	535.6	535.9	535.6
211	1184.081	6294.014	537.8	535.7	536.0	535.8	535.8	535.7
212	1213.665	6388.169	537.2		535.4	535.3	535.4	535.2
608	1040.489	6412.304	539.5		536.9	536.7		536.7
609	1100.292	6480.579	539.4		537.1	537.0		537.0
AH-02	1036.454	6056.311	539.6					
AH-03	1274.063	6018.17	537.8					
AH-04	1335.945	6095.279	537.5					
AH-05	1299.317	6126.092	537.5					
AH-06	1239.613	6089.831	538.1					
AH-07	1228.913	6175.698	538.0			535.9	535.5	535.2
AH-08	1230.697	6174.269	538.5			527.8		
AH-16	1380.503	6348.13	533.2					
AH-17	1375.018	6302.927	533.9					
AH-18	1410.451	6347.62	532.8					
AH-19	1375.075	6264.235	534.1					
AH-20	1163.704	6111.033	538.6					
HP-5	1064.741	6034.521	540.0					
HP-8	1143.426	6181.826	538.8					
HP-9	1165.531	6139.434	538.4					
HP-10	1112.278	6121.842	539.2					
HP-11	1112.143	6121.878	539.2					
HP-12	1335.556	6098.749	537.3					
HP-13	1236.667	6332.208	536.3					
HP-14	1375.086	6297.49	533.9					
HP-16	784.289	6281.187			534.8			
HP-17	913.106	6433.639				534.6		
HP-18	957.21	6410.506				529.6		
HP-19	988.893	6391.667				534.7		
HP-21	1116.379	6379.617	539.1					
HP-22	1155.887	6239.009	538.5			536.4		
HP-23	1315.361	6326.141	534.8			534.3		
HP-24	1289.408	6311.474	536.0			534.7		
HP-25	1236.657	6281.773	536.5			535.4		
HP-26	1275.728	6266.435	536.7			535.0		
N	1157.207	6114.663	538.8	536.9	537.1			

Table 5-2: Estimated Seepage Velocities

	Hydraulic Conductivity (m/s)	Gradient (m/m)	Specific Discharge (m/yr)	Seepage Velocity (m/yr)
Minimum	2.0×10^{-5}	0.9×10^{-2}	5.7	18.4
Maximum	1.0×10^{-4}	1.3×10^{-2}	41.0	132
Expected	7.5×10^{-5}	1.1×10^{-2}	26.0	83.9

Table 5-3: Estimated Retarded Contaminant Velocities

	Seepage Velocity (m/yr)	Retarded TCA Velocity (m/yr)	Retarded DCA Velocity (m/yr)	Retarded Benzene Velocity (m/yr)
Minimum	18.4	9.0	4.5	3.5
Maximum	132	64.7	32.2	25.4
Expected	83.9	40.0	20.5	16.2

Table 5-4: Calculation of the Biological Decay Rate Based on Buscheck and Alcantar (1995)

For TCA

Cases	**Groundwater Velocity V_x (m/yr)**	**Retardation Coefficient R**	**Contaminant Velocity V_c (m/yr)**	**Dispersivity α**	**k/v_x**	**λ (yr^{-1})**	**$t_{1/2}$ (yr)**	**$t_{1/2}$ (da)**
Case 1	83.9	2.04	41.1	20	-0.075	7.7	0.1	33
Case 2	**42.0**	2.04	20.6	20	-0.075	3.9	0.2	66
Case 3	83.9	2.04	41.1	**40**	-0.075	12.3	0.1	21
Case 4	83.9	**1.02**	82.3	20	-0.075	15.4	0.0	16
Case 5	83.9	**1.02**	82.3	**80**	-0.075	43.2	0.0	6
Case 6	83.9	2.04	41.1	20	-0.075	7.7	0.1	33

For DCA

Cases	**Groundwater Velocity V_x (m/yr)**	**Retardation Coefficient R**	**Contaminant Velocity V_c (m/yr)**	**Dispersivity α**	**k/v_x**	**λ (yr^{-1})**	**$t_{1/2}$ (yr)**	**$t_{1/2}$ (da)**
Case 1	83.9	4.11	20.4	30	-0.011	0.3	2.3	847
Case 2	**42.0**	4.11	10.2	30	-0.011	0.1	4.6	1694
Case 3	83.9	4.11	20.4	**60**	-0.011	0.4	1.9	679
Case 4	83.9	**2.06**	40.8	30	-0.011	0.6	1.2	424
Case 5	83.9	**2.06**	40.8	**120**	-0.011	1.0	0.7	243

Note: Bold values have been changed for each case

Table 5-5: Groundwater Geochemistry From Groundwater Sampling, November, 1999

Site	Flow-through Cell Temp °C	pH	Electrical Conductivity µS/cm	D.O. mg/L	eH mV	comments
Well 13	7.3	6.1	254	4.5	-288.27	
Well 17	13.2	6.8	305	4.4	-333.4	slow water inflow
Well 27	11.7	6.9	195	4.4	-309.3	
Well 204	9.4	6.9	681	4.4	-312.9	
Well 205	7.4	6.4	2860	1.6	-328.6	
Well 206	10.1	6.8	393	4.4	-291.8	
Well 210	10.9	6.7	109	4.3	-299.0	
Well 211	9.2	6.6	262	6.2	-303.7	
AH-7	10.1	6.7	6100	2.2	-311.0	
HP-27	11.5	6.8	766	7.1	-295.6	
HP-28	11.9	6.6	616	0.9	-298.3	only one reading
HP-29	11.1	6.8	484	6.1	-285.4	only one reading
HP-30	10.1	6.6	527	7.0	-320.8	only one reading
HP-31	11.8	6.7	333	7.2	-277.8	only one reading
HP-32	12.1	6.4	545	1.3	-284.0	only one reading
HP-33	14.3	6.8	1264	6.8	-276.3	only one reading
HP-35	10.7	6.6	525	6.8	-292.6	only one reading
HP-36	10.5	6.3	61610	6.8	-298.5	only one reading, difficult to obtain water
HP-37	10.2	7.1	1809	6.7	-320.7	only one reading
HP-38	10.1	6.3	5090	6.6	-245.6	only one reading
HP-39	10.9	6.5	4660	6.5	-327.6	only one reading
HP-40	10.5	6.5	3690	4.0	-335.8	only one reading
HP-41	9.9	6.6	4540	11.9	-333.6	only one reading
HP-42	11.6	6.5	609	7.1	-296.4	only one reading
HP-43	11.5	6.7	596	7.0	-301.5	only one reading
HP-45	11.8	6.2	3660	6.3	-320.5	only one reading

Note: Wells sampled with bladder pump and flow-through cell
Hydropunch samples (HP) sampled with Waterra pump and flow-through cell

Table 5-6: Groundwater Contaminant Concentrations, November, 1999

	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	Xylenes (µg/L)	Σ BTEX (µg/L)	1,1,1-TCA (µg/L)	1,1-DCA (µg/L)	DCBs (µg/L)	VC (µg/L)
Site									
Well 7	190	450	13	1100	1753	n/a	n/a	n/a	n/a
Well 13	< 1	< 1	< 1	< 1	0	< 1	< 1	< 1	< 2
Well 17	1000	8600	1100	7200	17900	2100	470	< 100	< 200
Well 27	1400	5800	1100	7600	15900	9700	1900	< 100	< 200
Well 27 Duplicate	1400	5700	1000	7500	15600	9400	1800	< 100	< 200
Well 27 Rinsate	1	4	< 1	< 1	5	4	1	< 1	< 2
Well 27 Field	< 1	2	< 1	< 1	2	2	< 1	< 1	< 2
Well 204	< 100	62	< 100	670	732	1100	440	59	< 200
Well 205	450	870	130	3400	4850	550	2400	< 100	<200
Well 206	370	730	< 100	2300	3400	950	880	< 100	< 200
Well 210	270	290	< 10	690	1250	120	380	42	< 20
Well 211	< 1	< 1	< 1	< 1	0	< 1	< 1	< 1	< 2
AH-7	890	2600	200	4900	8590	4300	1200	< 100	< 200
HP-27	450	9000	1500	8300	19250	2500	160	< 100	< 200
HP-28	2000	10000	1500	7800	21300	2500	450	< 100	< 200
HP-28 Duplicate	2200	11000	1200	6600	21000	2600	460	< 100	< 200
HP-29	< 1	< 1	< 1	< 1	0	< 1	< 1	< 1	< 2
HP-30	2	2	9	59	72	5	32	4	< 2
HP-31	< 10	< 10	< 10	1160	1160	< 10	< 10	36	< 20
HP-32	270	2200	300	4200	6970	3700	120	< 100	< 200
HP-32 Rinsate	< 1	2	2	27	31	1	< 1	1	< 2
HP-32 Field	< 1	1	< 1	< 1	1	2	< 1	< 1	< 2
HP-33	59	4700	370	2880	8009	3300	290	< 100	< 200
HP-34	1200	2900	570	6400	11070	11000	1000	< 100	< 200
HP-35	4	< 1	8	472	484	2	6	< 1	< 2
HP-36	430	2500	240	2400	5570	8600	890	< 100	< 200
HP-37	< 100	3000	580	5000	8580	1900	520	< 100	< 200
HP-38	< 100	3500	130	2200	5830	5000	660	< 100	< 200
HP-39	< 100	3700	180	2150	6030	5200	660	< 100	< 200
HP-39 Duplicate	< 100	3800	200	2300	6300	5200	710	< 100	< 200
HP-40	< 100	600	< 100	1320	1920	1200	390	< 100	< 200
HP-41	< 100	1800	110	1220	3130	1800	750	< 100	< 200
HP-42	1800	10000	1400	8100	21300	2200	380	< 100	< 200
HP-43	1500	8000	1200	7100	17800	< 100	970	< 100	< 200
HP-44	460	3500	620	7800	12380	4400	820	< 100	< 200
HP-45	480	1700	160	2400	4740	1300	1100	< 100	< 200
HP-45 Rinsate	< 1	1	< 1	< 1	1	2	< 1	< 1	< 2
HP-45 Field	< 1	< 1	< 1	< 1	0	< 1	< 1	< 1	< 2
Well N	1100	3900	130	1040	6170	2500	660	< 100	< 200

1. n/a = no sample taken
2. Rinsate blanks = distilled water collected by rinsing already cleaned sampling equipment (to check efficiency of cleaning system)
3. Field blanks = distilled water collected in sample bottles and left open to the atmosphere near the sampling sites (to check effect of volatilization on sampling)
4. The symbol "<" indicates value less than detection limit

Table 5-7: Interim Assessment Criteria for Soil and Water (Modified From CCREM, 1991)

Parameter	**Soil ug/g**	**Water ug/L**
pH	6 to 8	none
conductivity	2 dS/m	none
Monocyclic Aromatic Hydrocarbons		
benzene	0.05	0.5
ethylbenzene	0.1	0.5
toluene	0.1	0.5
xylene	0.1	0.5
1,2-DCB	0.1	0.2
1,3-DCB	0.1	0.2
1,4-DCB	0.1	0.2
chlorinated aliphatics (each) includes 1,1-DCA and 1,1,1-TCA	0.1	0.1

Table 5-8: Remediation Criteria for Water (Modified From CCREM, 1991; Health and Welfare, 1996)

Parameter	**Drinking Water µg/L unless otherwise stated**
DO	none
pH	6.5 - 8.5
Inorganic Parameters	
chloride (total)	≤250 mg/L
iron	≤300
manganese	≤50
nitrate	45 mg/L
nitrite	4.5 mg/L
Organic Parameters	
benzene	5
ethylbenzene	≤2.4
toluene	≤24
xylene	≤300
1,2-DCB	200;≤3
1,3-DCB	none listed
1,4-DCB	5;≤1
chlorinated aliphatics (each)	none listed

Table 5-9: Chemical Properties of Compounds

Compound	Solubility µg/L	log K_{ow}	log k_{oc}	Henry's constant atm m^3/mol
Benzene C_6H_6	1750 x 10^3	2.12	1.94	5.40x10^3
1,1-DCA $C_2H_4Cl_2$	5500 x 10^3	1.84 1.79$^{(1)}$	1.81 1.47$^{(1)}$	1.80 x10^2
1,1,1-TCA $C_2H_3Cl_3$	1550 x 10^3 1485 x $10^{3(2)}$	2.47	2.18	5.43 x 10^3
1,2-DCB $C_6H_4Cl_2$	100 x 10^3	3.4	2.26	1.90x10^3
1,3-DCB $C_6H_4Cl_2$	123 x 10^3	3.38	2.23	3.60x10^3
1,4-DCB $C_6H_4Cl_2$	79 x 10^3	3.39	2.2	3.10x10^3
Ethylbenzene C_8H_{10}	152 x 10^3	3.13	2.2	6.60x10^3
Toluene C7H8	515 x 10^3	2.65	2.18	6.70x10^3
Vinyl Chloride C_2H_3Cl	1100 x 10^3	0.6	0.39	1.22 x 10^3

All From Montgomery et al., 1990 except footnoted

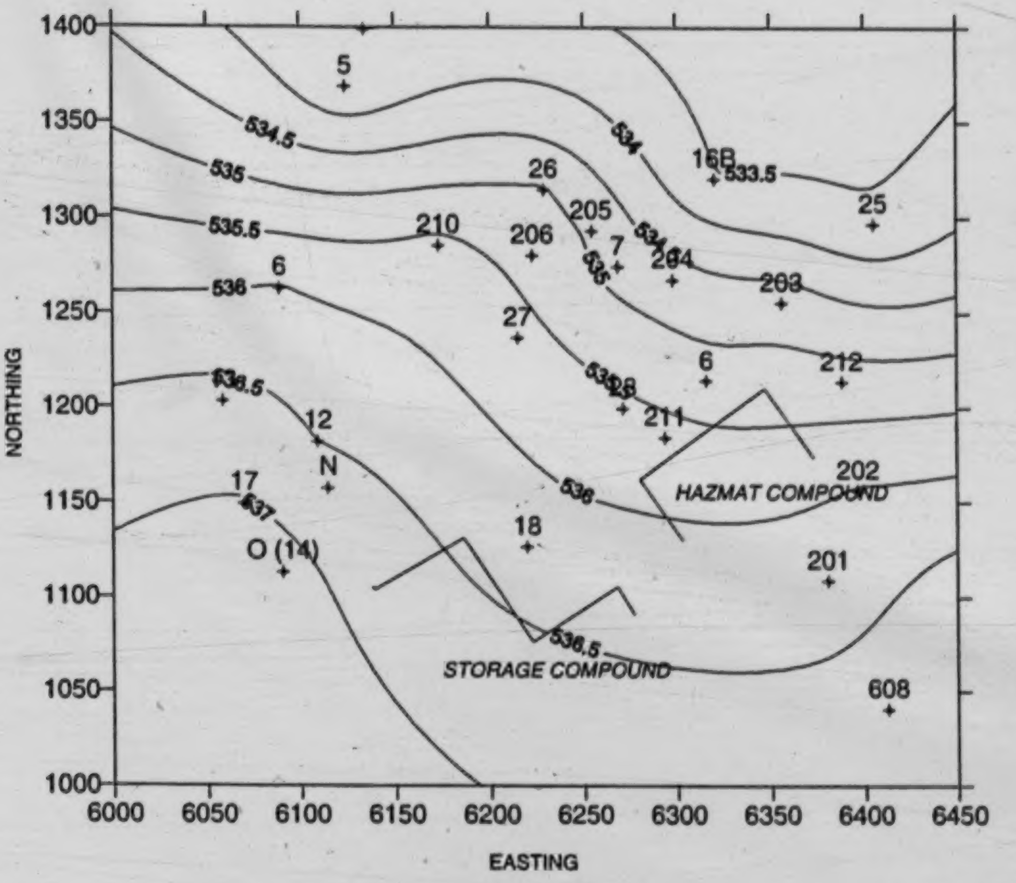
[1] From Ma et al.1990

[2] Horvath, 1982

Table 5-10: Soil Contaminant Concentrations, November, 1999

		Benzene	Toluene	Ethylbenzene	Xylenes	Σ BTEX	1,1,1-TCA	1,1-DCA	DCBs	VC	
Site		(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	(μg/kg)	
Well N	top	2000	20000	11000	80000	113000	29000	< 1000	< 1000	< 2000	
Well N	base	110	480	150	1230	1970	450	58	32	< 60	
Well 27	top	< 150	970	< 150	19200	20170	4700	210	1600	< 300	2 m South (upgradient) from Well 27
Well 27	middle	120	440	31	330	921	540	280	< 30	< 60	
Well 27	base	< 30	100	< 30	340	440	180	32	41	< 60	
Well 27	top	< 150	360	< 150	54000	54360	6100	240	3300	< 300	10-15 m downgradient of Well 27
Well 27	middle	35	140	< 30	30	205	180	< 30	< 30	< 60	
Well 27	base	32	110	< 30	37	179	120	32	< 30	< 60	
Well 27	top	< 150	570	< 150	22800	23370	3400	< 150	2100	< 300	1 m NW of Well 27 (cross gradient)
Well 27	middle	54	230	< 30	166	450	130	< 30	< 30	< 60	
Well 27	base	100	290	< 30	225	615	520	130	< 30	< 60	

Note: Where concentration is reported to be less than a certain value, that value was reported by the commercial laboratory as the detection limit for that sample

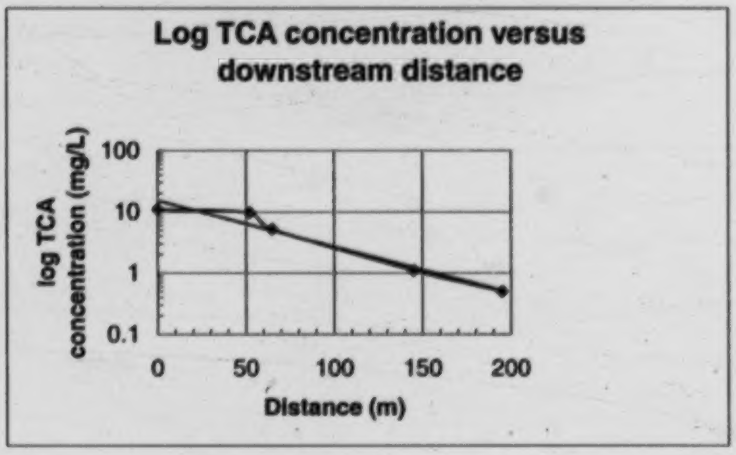


1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING
534.5
535
535.5
536
536.5
537
534
533.5
5
16B
25
26
205
210
206
7
204
203
6
27
6
212
28
211
12
N
202
17
18
O (14)
201
608
HAZMAT COMPOUND
STORAGE COMPOUND

Figure 5-1: Groundwater Table Elevations, July 1999

Figure 5-2: Log Contaminant Concentrations Versus distance for TCA and Calculation of Biodegradation Rate Based on Buschek and Alcantar (1995), November, 1999

Distance (m)	TCA conc. (mg/L)	sample point
0	11	HP-34
52	9.7	27
65	5.2	HP-39
145	1.1	204
195	0.5	HP-23



$$\boxed{\lambda \equiv \frac{v_c}{4\alpha_x}\left(\left[1+2\alpha_x\left(\frac{k}{v_x}\right)\right]^2-1\right)}$$

k/v_x = slope of regression line = -0.075

v_c = 41 m/yr.(calculated in Appendix D)

α_x = longitudinal dispersivity

= typically estimated as $\alpha_x = 0.1 \times$ plume length (Domenico and Schwartz, 1990)

For a plume length of 200 m,

$\alpha_x = 0.1 \times 200$ m = 20 m

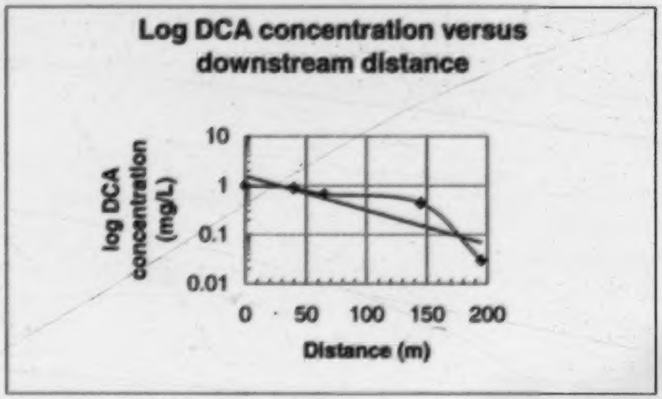
$$\boxed{\lambda \equiv \frac{41}{4(20)}\left(\left[1+2(20)(-0.075)\right]^2-1\right)}$$

$\lambda = 1.54\ \text{yr}^{-1}$

Using $k/v_x = 0.075$, $\lambda = 7.69\text{yr}^{-1}$

Figure 5-3: Log Contaminant Concentrations Versus distance for DCA and Calculation of Biodegradation Rate Based on Buschek and Alcantar (1995), November, 1999

Distance (m)	DCA conc. (mg/L)	sample point
0	1	HP-34
40	0.89	HP-36
65	0.66	HP-39
145	0.44	204
195	0.03	HP-23



$$\boxed{\lambda \equiv \frac{v_c}{4\alpha_x}\left(\left[1+2\alpha_x\left(\frac{k}{v_x}\right)\right]^2-1\right)}$$

k/v_x = slope of regression line = -0.011

$k_{oc(DCA)} = 10^{1.81} = 64.6$ L/kg (Montgomery et al., 1990)
$f_{oc} = 0.007$

$k_d = f_{oc}k_{oc}$
$= 0.452$ L/kg

$\rho_b = 2.13$ kg/L (calculated in Appendix D)
R = 4.11
$v_c = 20.4$ m/yr (calculated in Appendix D)

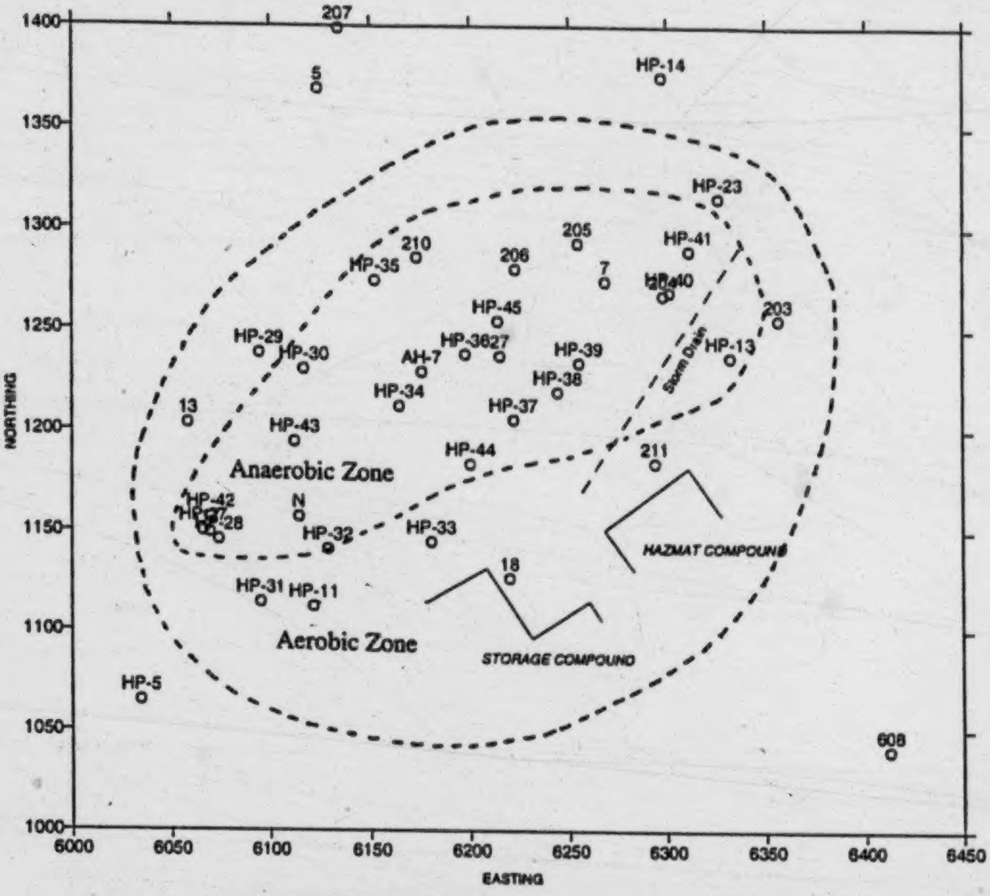
For a plume length of 300 m,
$\alpha_x = 0.1 \times 300\text{ m} = 30\text{ m}$

There is uncertainty about the plume length because the isopleth for 1,1-DCA is not well defined. From Figure 9-5, a plume length of approximately 300 m seems reasonable.

$$\boxed{\lambda \equiv \frac{20}{4(30)}\left([1+2(30)(-0.011)]^2-1\right)}$$

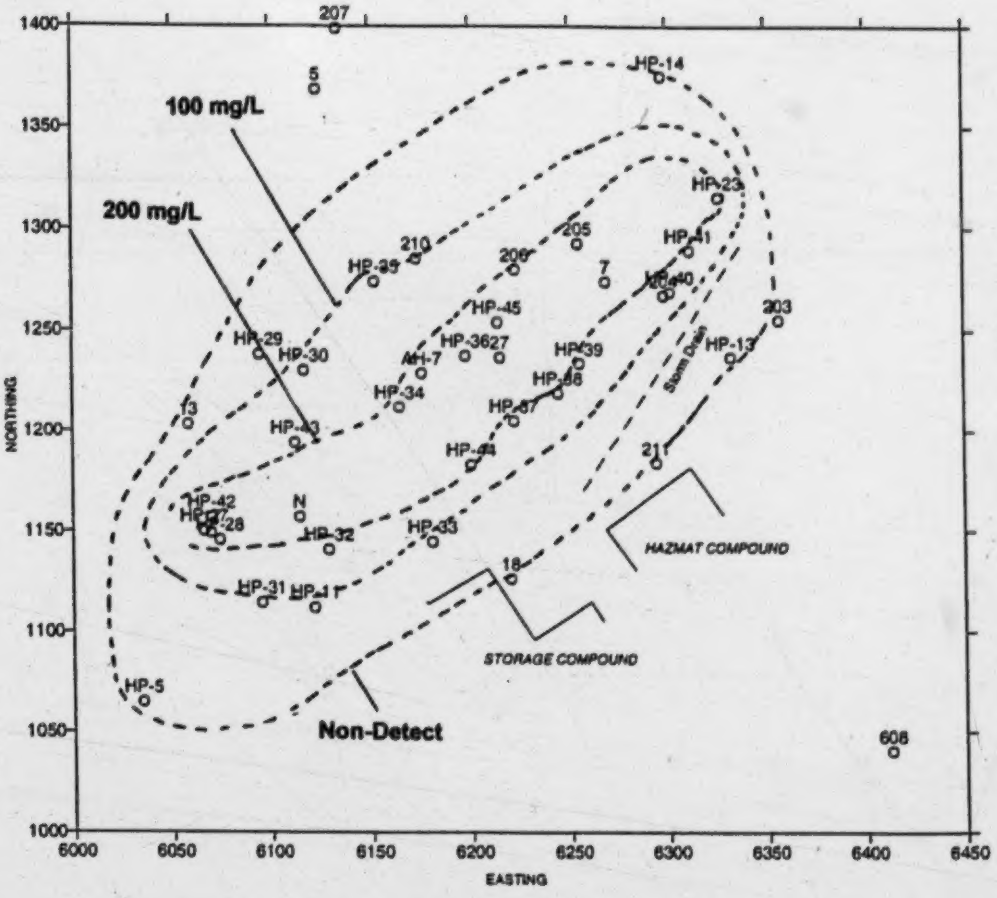
$\lambda = -0.15\text{ yr}^{-1}$

Using $k/v_x = 0.011$, $\lambda = .293\text{yr}^{-1}$



207
5
HP-14
HP-23
210
205
HP-41
HP-35
206
7
HP-40
203
HP-45
HP-29
HP-30
HP-36
27
HP-39
HP-13
AH-7
HP-38
Storm Drain
HP-34
13
HP-37
HP-43
211
HP-44
Anaerobic Zone
HP-42
N
28
HP-32
HP-33
HAZMAT COMPOUND
18
HP-31
HP-11
Aerobic Zone
STORAGE COMPOUND
HP-5
608
1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING

Figure 5-4: Aerobic and Anaerobic Zones Across the Site, November 1999



100 mg/L
200 mg/L
Non-Detect
HAZMAT COMPOUND
STORAGE COMPOUND
Storm Drain
207
5
HP-14
HP-23
HP-41
HP-40
204
205
206
210
HP-35
7
203
HP-45
HP-36
27
HP-39
HP-13
AH-7
HP-29
HP-30
HP-34
HP-38
HP-37
13
HP-43
HP-44
211
HP-42
HP-27
HP-28
N
HP-32
HP-33
18
HP-31
HP-11
HP-5
608
NORTHING
EASTING
1400
1350
1300
1250
1200
1150
1100
1050
1000
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450

Figure 5-5: Iron (II) Distribution (mg/L), November 1999

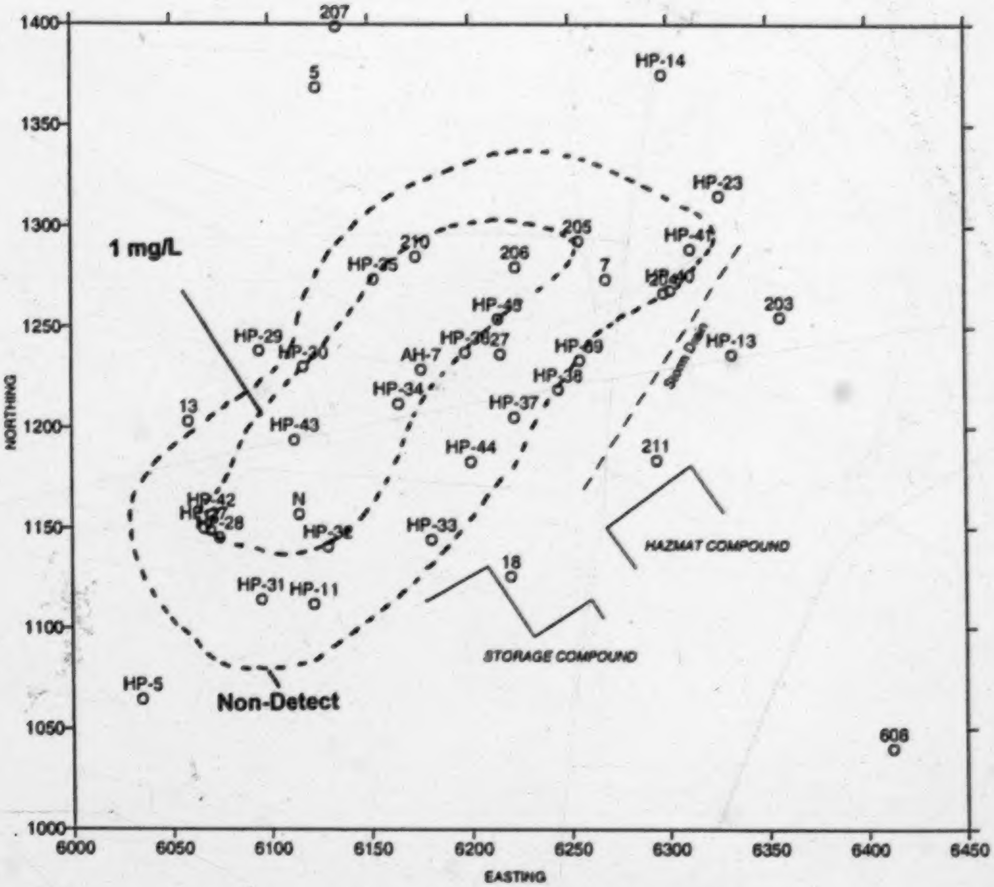

207
5
HP-14
HP-23
1 mg/L
210
HP-25
206
205
7
HP-41
HP-40
HP-48
203
HP-29
HP-30
HP-26
27
AH-7
HP-39
HP-13
HP-34
HP-38
HP-37
13
HP-43
HP-44
211
HP-42
N
HP-28
HP-32
HP-33
HAZMAT COMPOUND
18
HP-31
HP-11
STORAGE COMPOUND
HP-5
Non-Detect
608
NORTHING
1400
1350
1300
1250
1200
1150
1100
1050
1000
EASTING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450

Figure 5-6: Methane Distribution (mg/L), November 1999

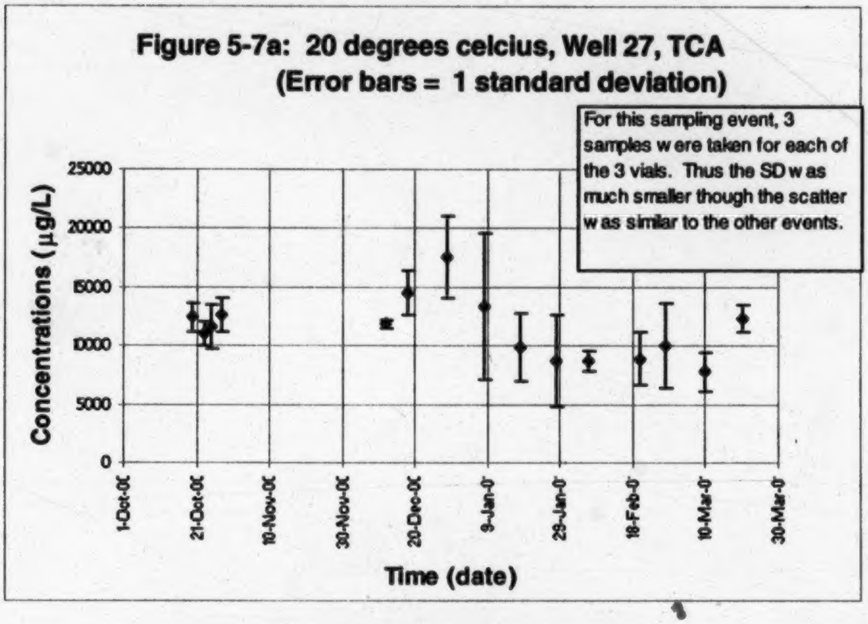


Figure 5-7a: 20 degrees celcius, Well 27, TCA (Error bars = 1 standard deviation)

For this sampling event, 3 samples w ere taken for each of the 3 vials. Thus the SD w as much smaller though the scatter w as similar to the other events.

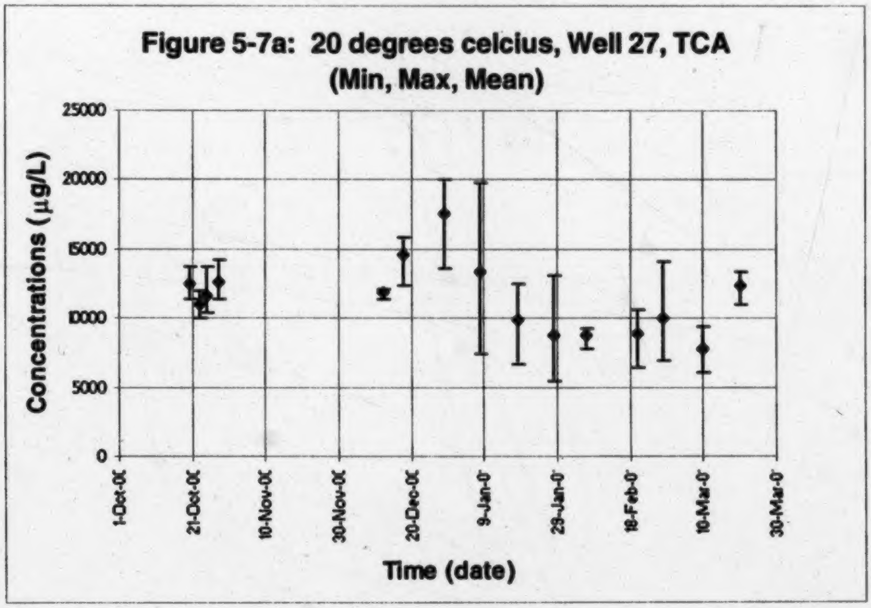


Figure 5-7a: 20 degrees celcius, Well 27, TCA (Min, Max, Mean)

Figure 5-7b: 20 degrees celcius, Well 27, DCA
(Error bars = 1 standard deviation)

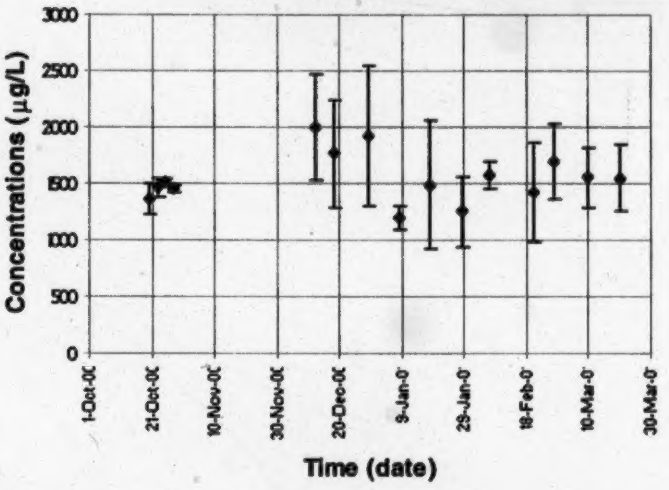
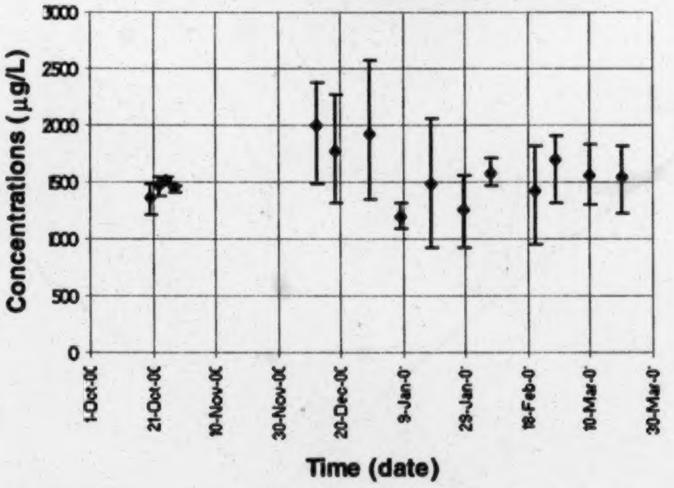


Figure 5-7b: 20 degrees celcius, Well 27, DCA
(Min, Max, Mean)



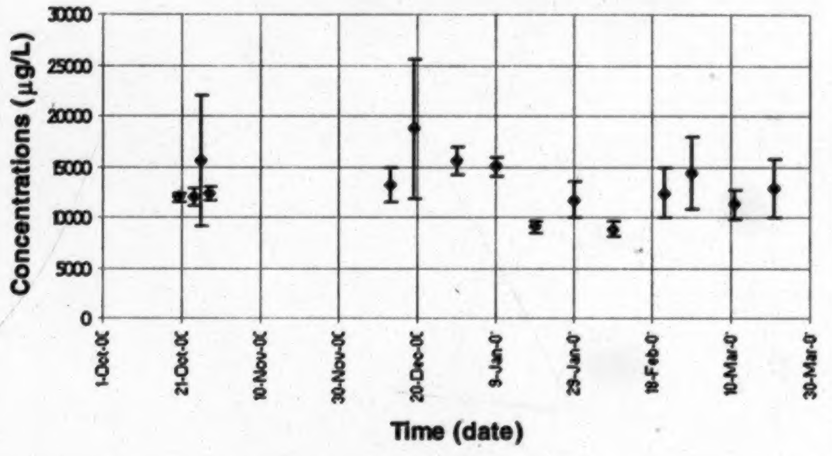


Figure 5-8a: 10 degrees celcius, Well 27, TCA (Error bars = 1 standard deviation)

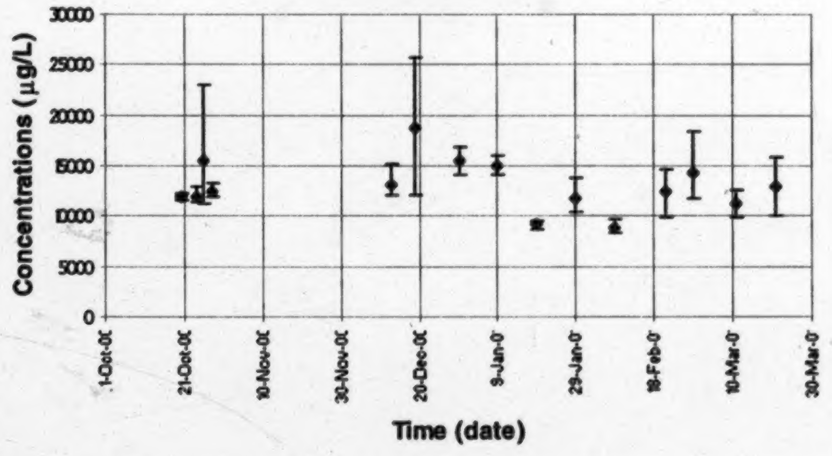


Figure 5-8a: 10 degrees celcius, Well 27, TCA (Min, Max, Mean)

Figure 5-8b: 10 degrees celcius, Well 27, DCA (Error bars = 1 standard deviation)

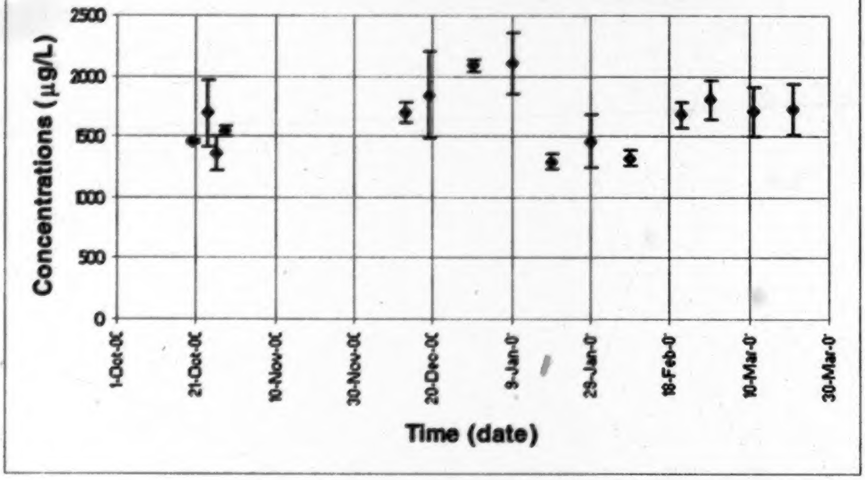


Figure 5-8b: 10 degrees celcius, Well 27, DCA (Min, Max, Mean)

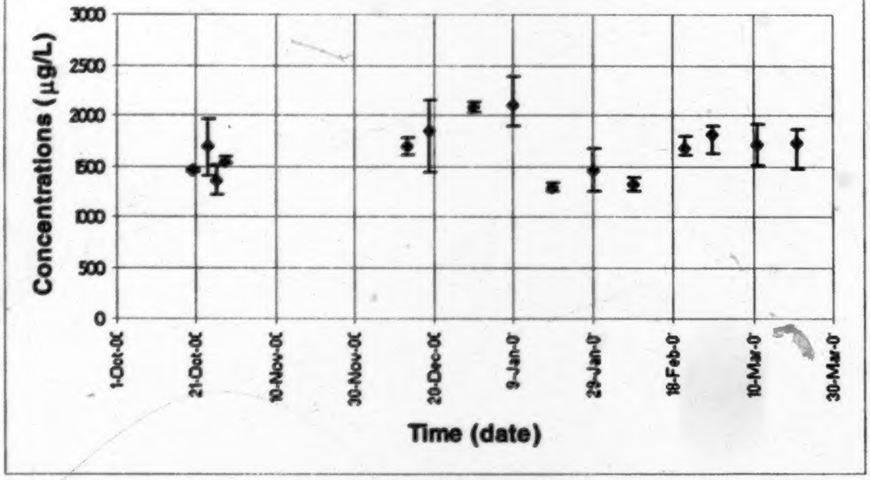


Figure 5-9a: 20 degrees celcius, Well N, TCA
(Error bars = 1 standard deviation)

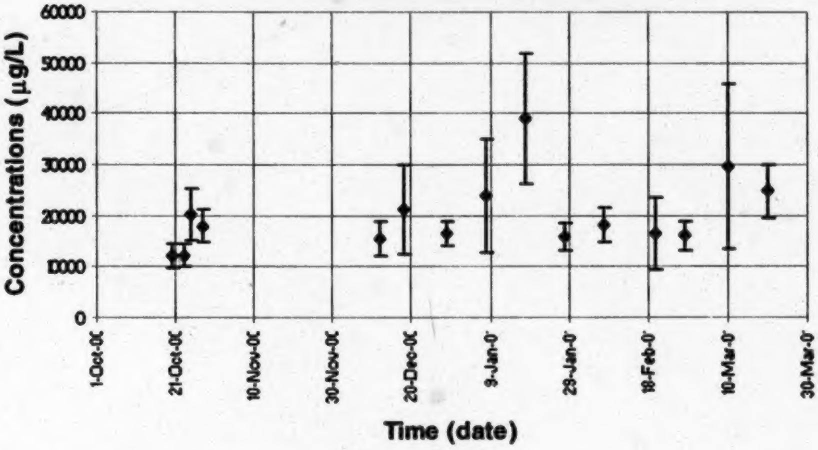
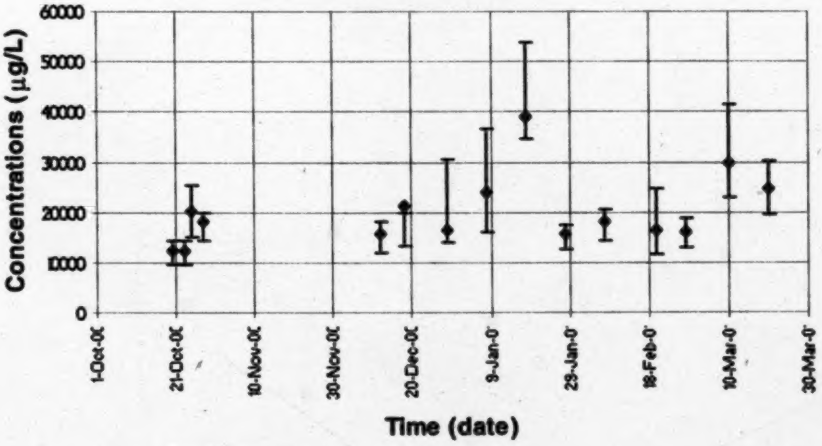


Figure 5-9a: 20 degrees celcius, Well N, TCA
(Min, Max, Mean)



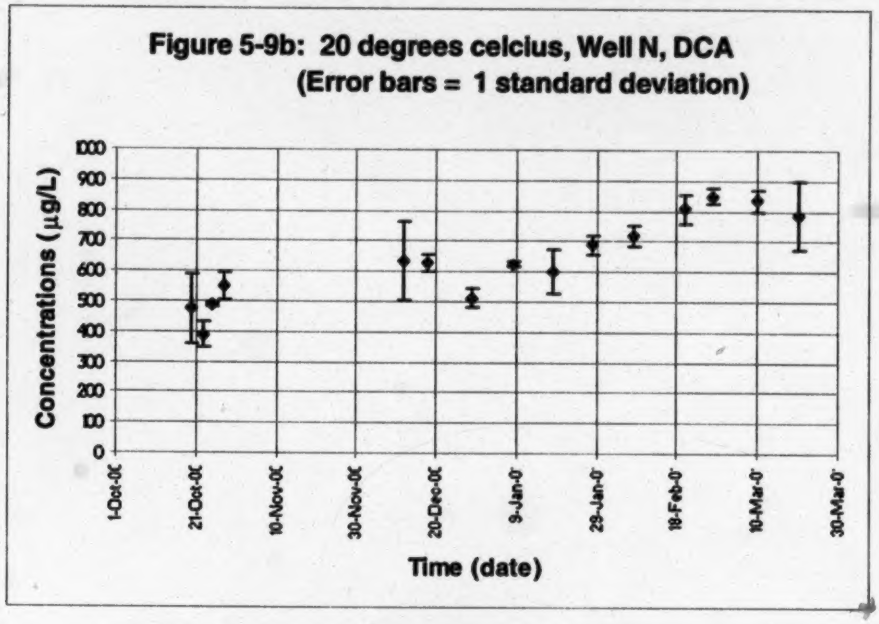


Figure 5-9b: 20 degrees celcius, Well N, DCA
(Error bars = 1 standard deviation)

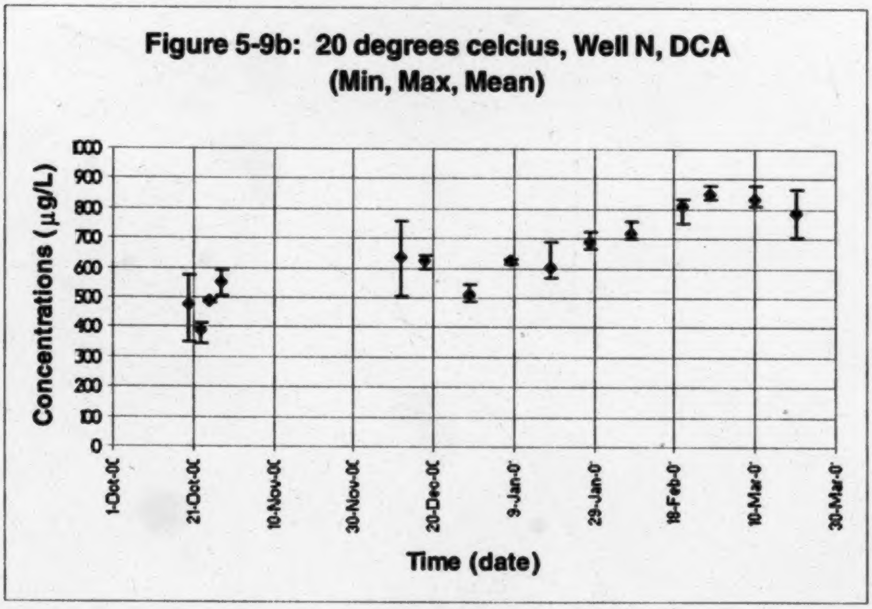


Figure 5-9b: 20 degrees celcius, Well N, DCA
(Min, Max, Mean)

Figure 5-10a: 10 degrees celcius, Well N, TCA
(Error bars = 1 standard deviation)

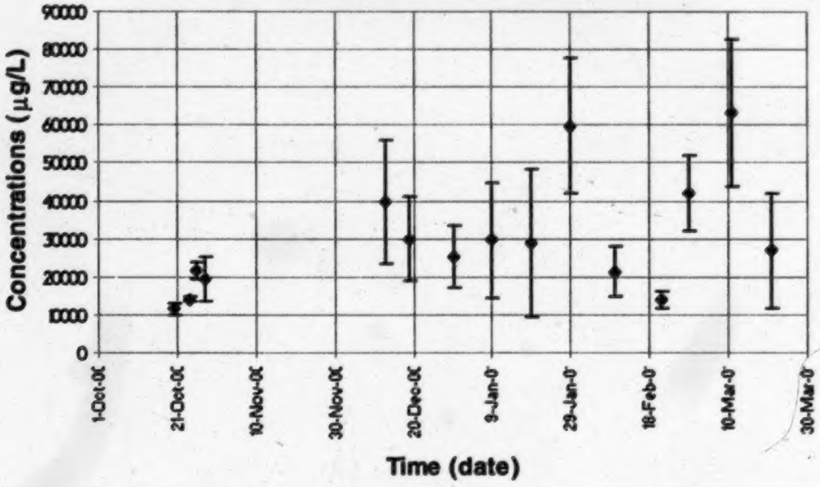


Figure 5-10a: 10 degrees celcius, Well N, TCA
(Min, Max, Mean)

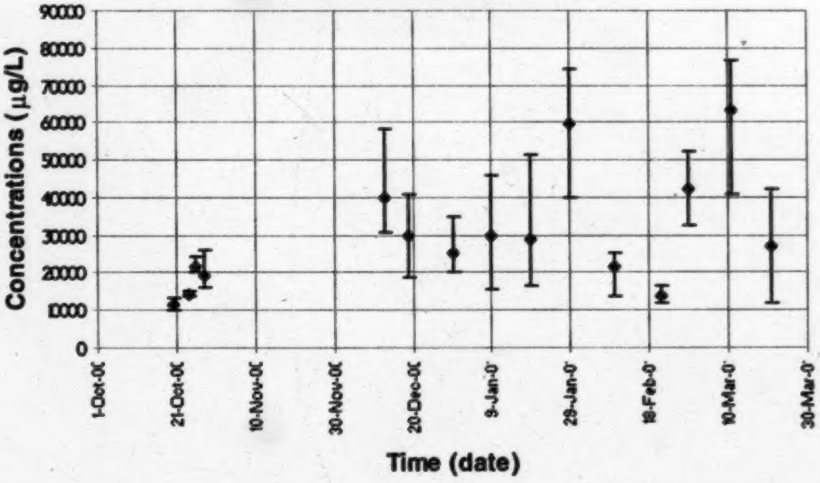


Figure 5-10b: 10 degrees celcius, Well N, DCA (Error bars = 1 standard deviation)

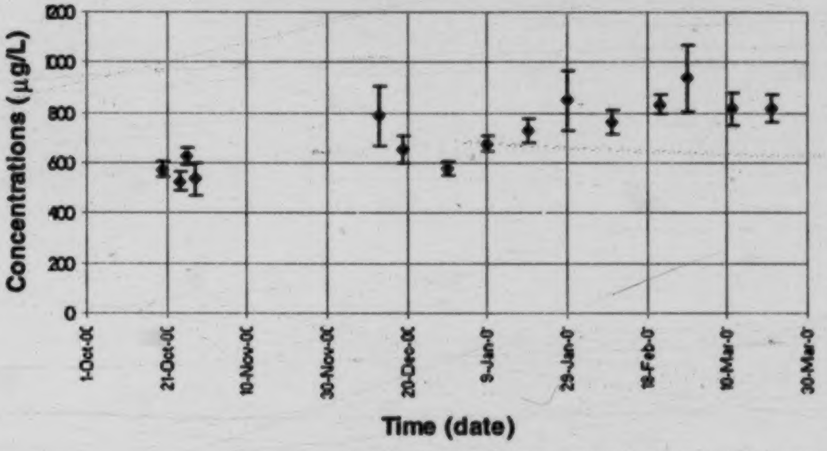
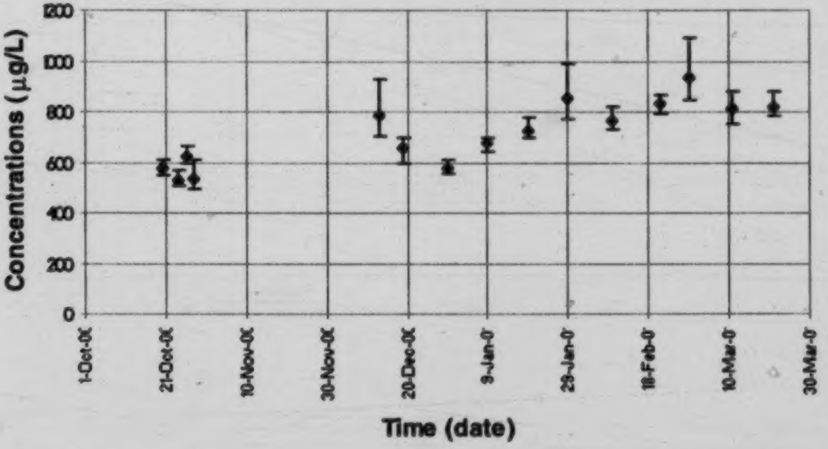


Figure 5-10b: 10 degrees celcius, Well N, DCA (Min, Max, Mean)



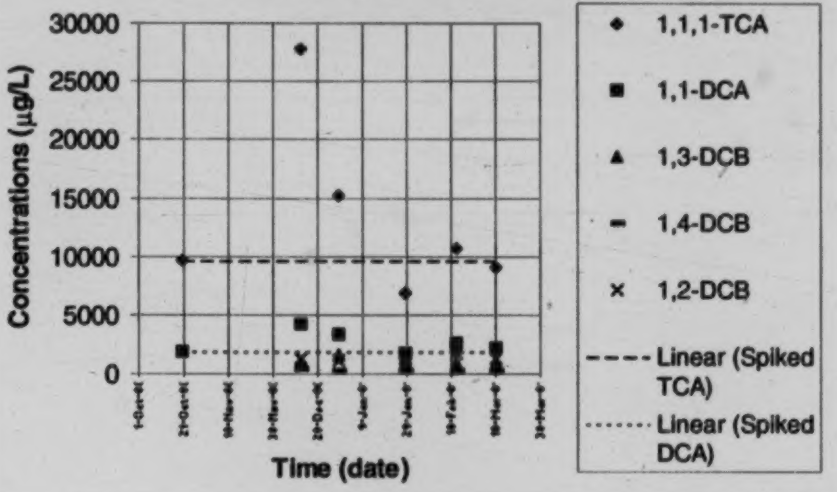


Figure 5-11: Negative Controls
20 degrees celcius, well 27

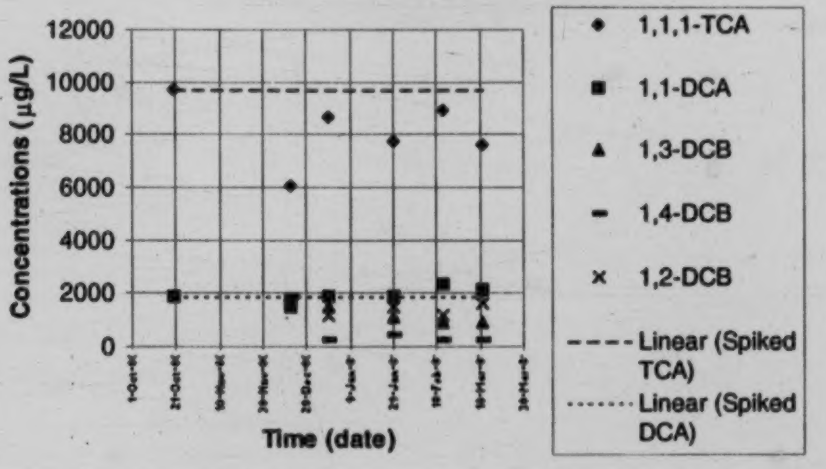


Figure 5-12: Negative Controls
10 degrees celcius, well 27

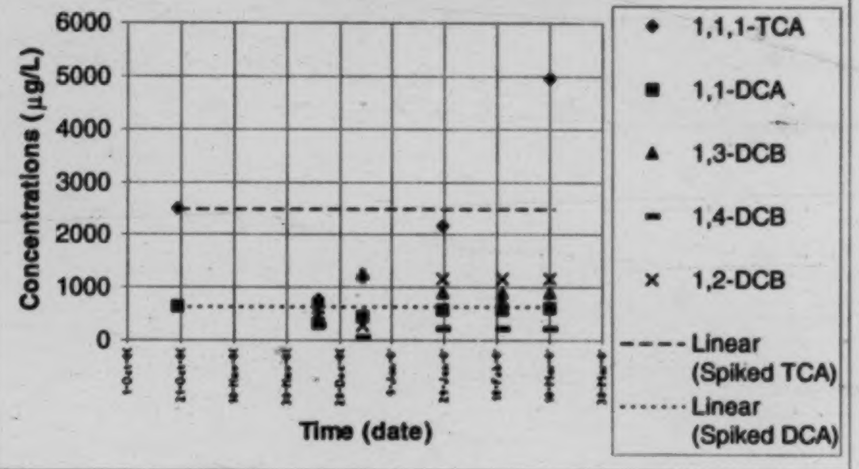


Figure 5-13: Negative Controls 20 degrees celcius, well N

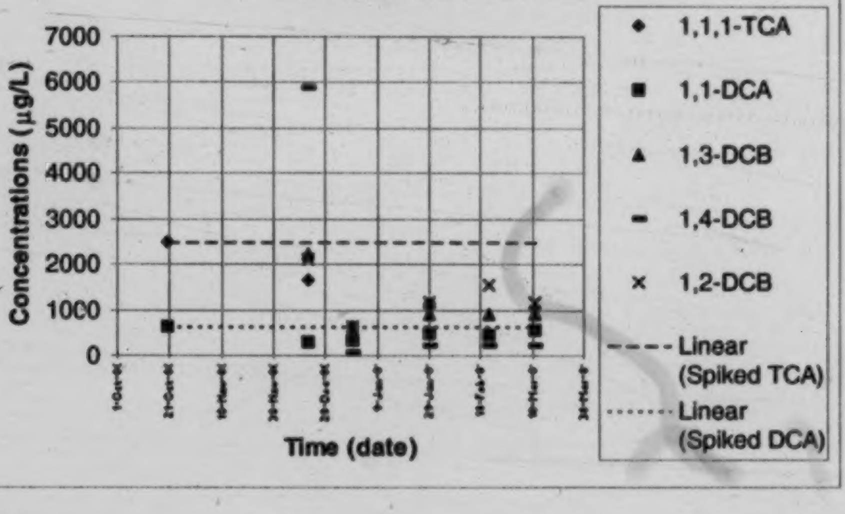


Figure 5-14: Negative Controls 10 degrees celcius, well N

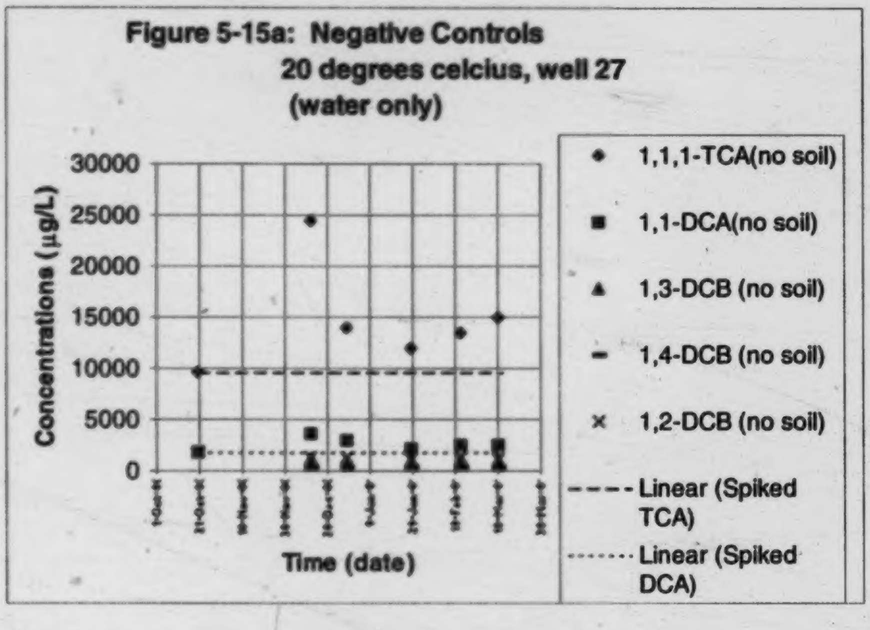


Figure 5-15a: Negative Controls
20 degrees celcius, well 27
(water only)

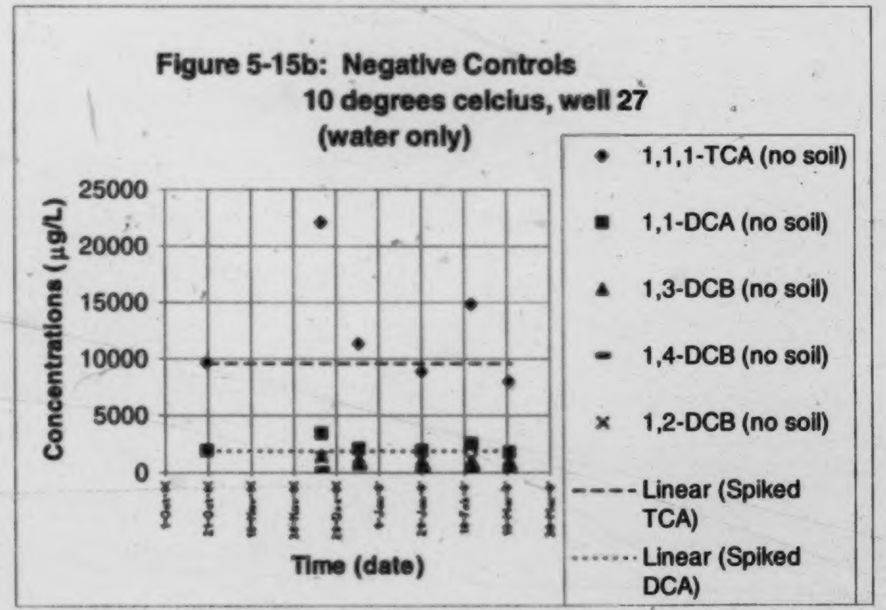


Figure 5-15b: Negative Controls
10 degrees celcius, well 27
(water only)

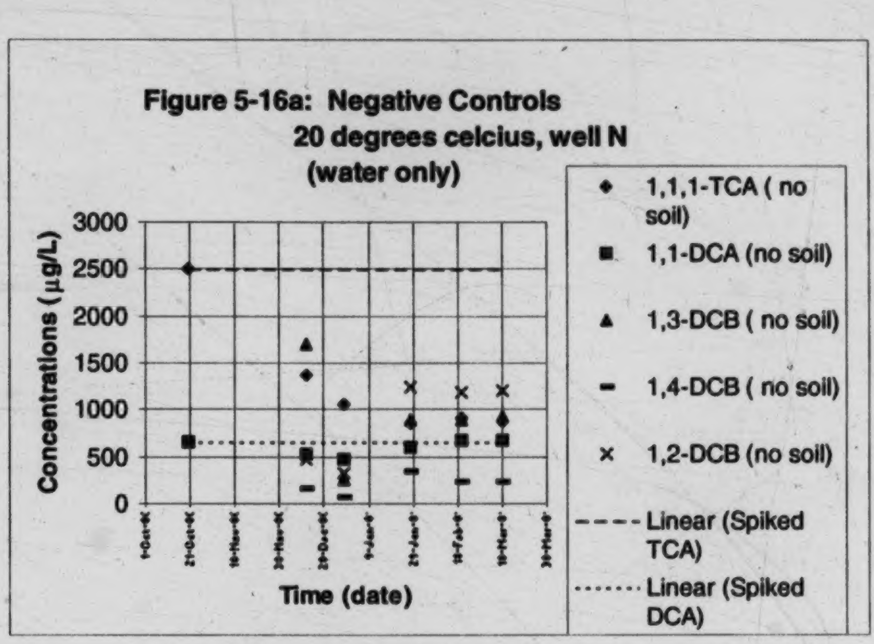


Figure 5-16a: Negative Controls
20 degrees celcius, well N
(water only)

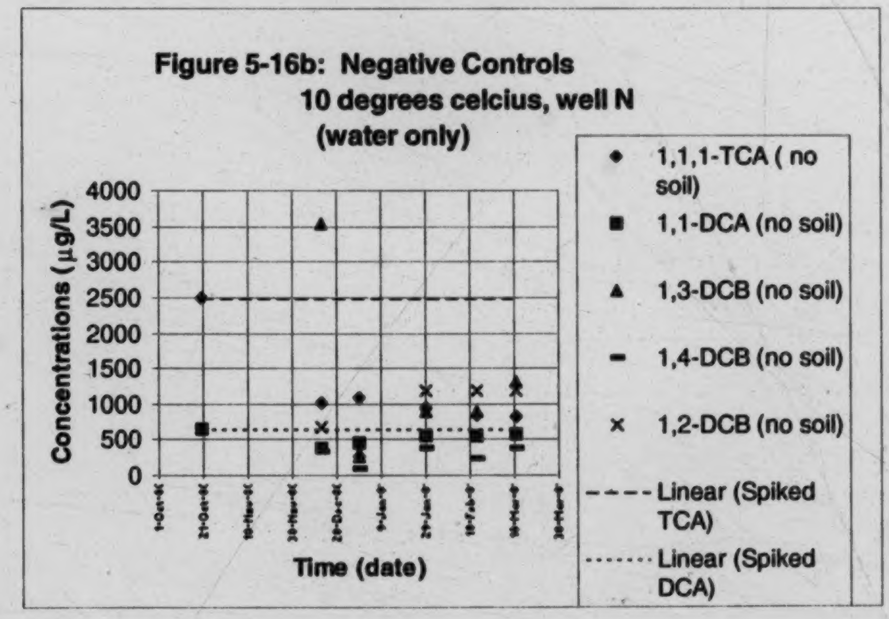


Figure 5-16b: Negative Controls
10 degrees celcius, well N
(water only)

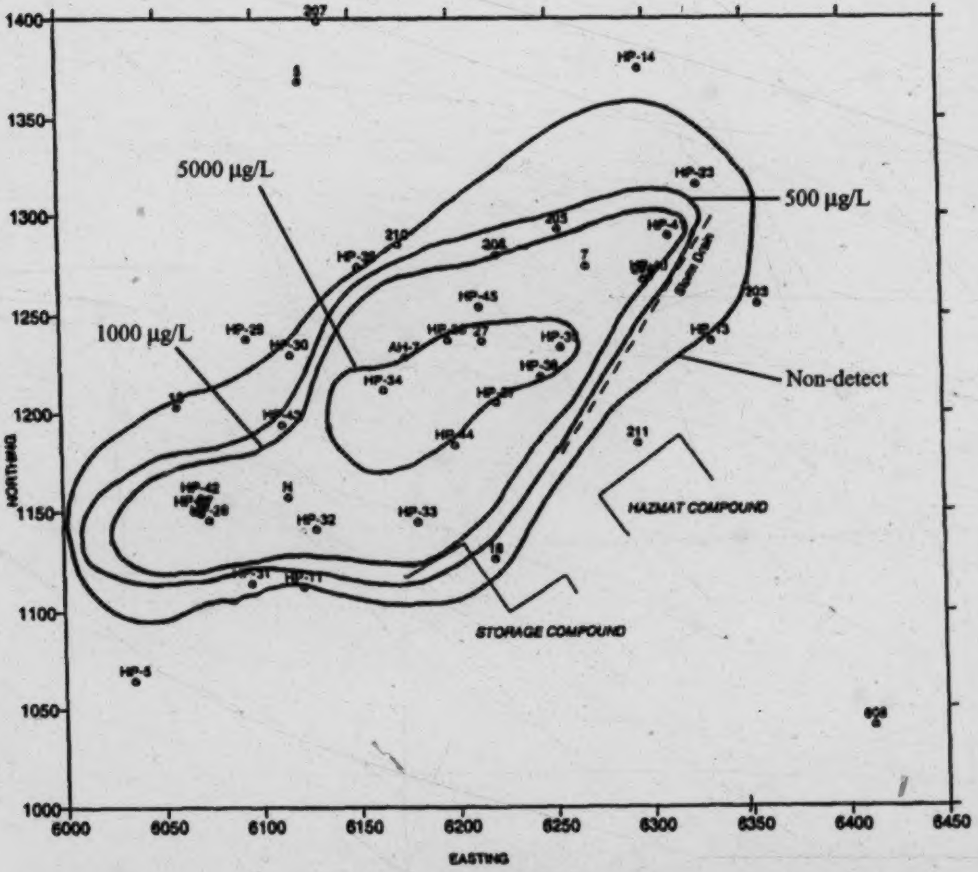

1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING
5000 µg/L
1000 µg/L
500 µg/L
Non-detect
207
HP-14
HP-23
203
210
HP-38
206
7
HP-4
HP-45
203
HP-29
HP-30
AH-7
27
HP-37
HP-36
HP-13
HP-34
HP-27
19
HP-43
HP-44
211
HP-42
HP-32
HP-33
18
HP-31
HP-11
HAZMAT COMPOUND
STORAGE COMPOUND
HP-5
608

Figure 5-17: TCA Concentrations (µg/L), from November 1999 Sampling, Zero Contour From Mullick 1999, C.I. = Irregular

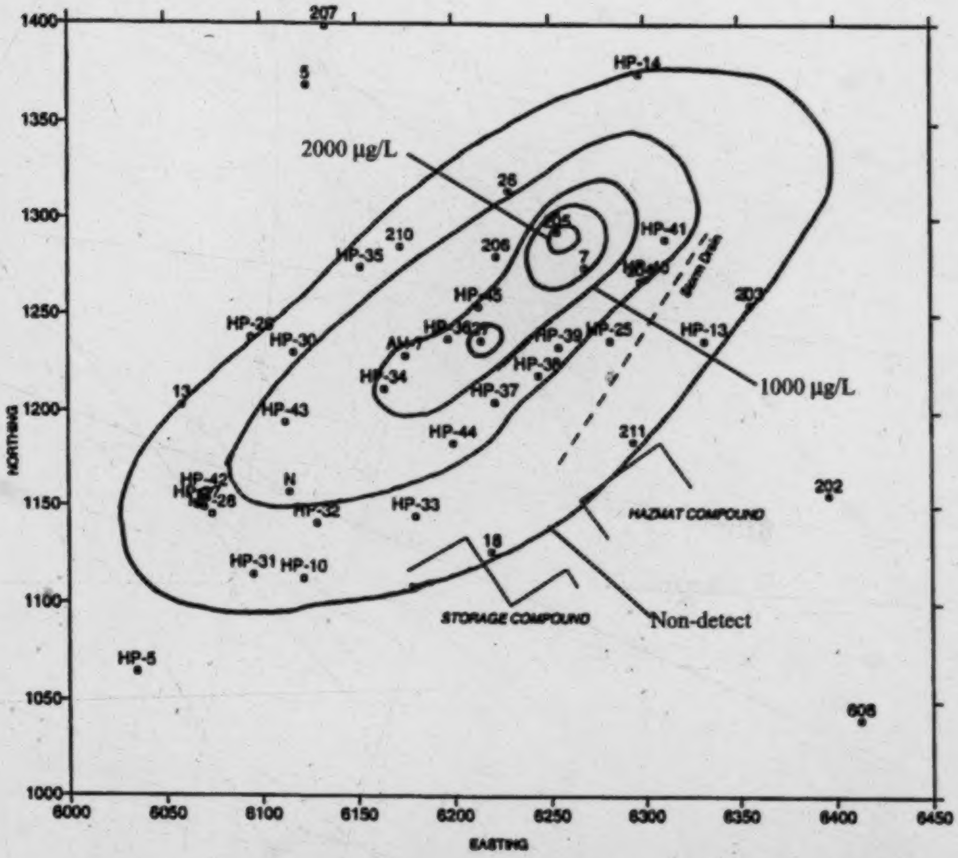

1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING
207
5
HP-14
2000 µg/L
26
210
HP-35
206
205
7
HP-41
HP-40
Storm Drain
203
HP-45
HP-28
HP-30
HP-36
27
AM-7
HP-39
HP-25
HP-13
HP-34
HP-38
HP-37
1000 µg/L
13
HP-43
HP-44
211
HP-42
N
202
HP-33
HP-32
HAZMAT COMPOUND
18
HP-31
HP-10
STORAGE COMPOUND
Non-detect
HP-5
606

Figure 5-18: DCA Concentrations (µg/L), from November 1999 Sampling, Zero Contour From Mullick 1999, C.I. = 500

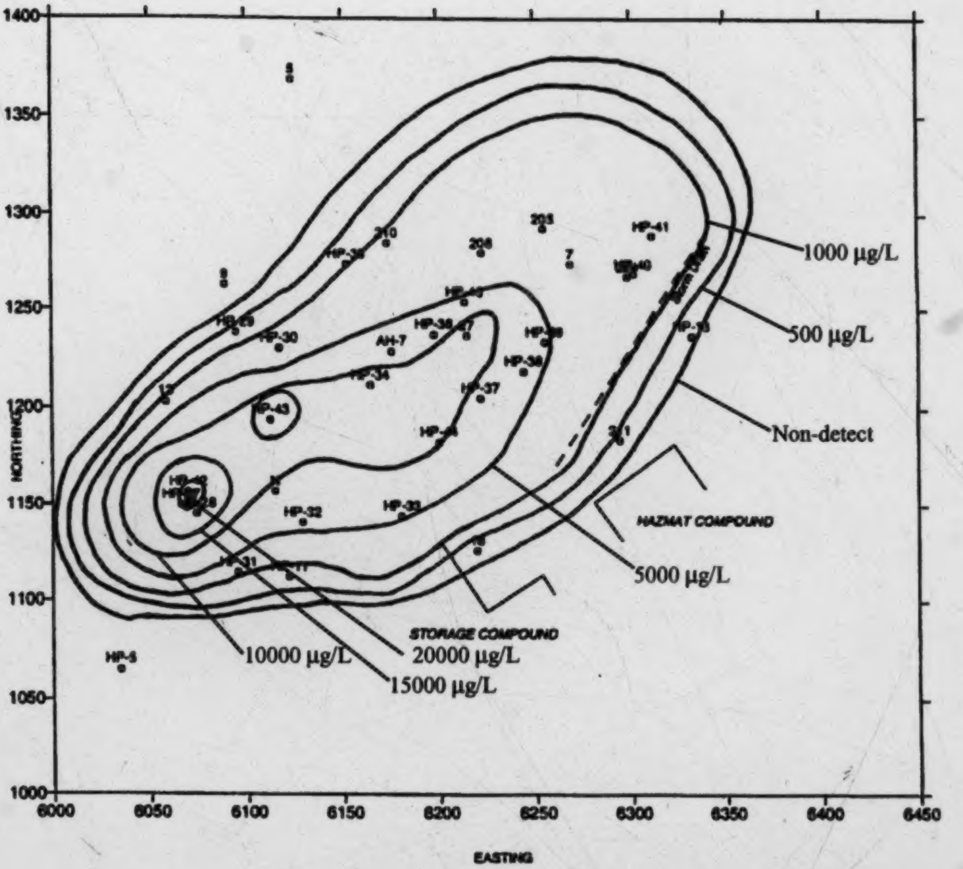

1400
1350
1300
1250
1200
1150
1100
1050
1000
NORTHING
6000
6050
6100
6150
6200
6250
6300
6350
6400
6450
EASTING
1000 µg/L
500 µg/L
Non-detect
5000 µg/L
10000 µg/L
20000 µg/L
15000 µg/L
HAZMAT COMPOUND
STORAGE COMPOUND
HP-41
HP-40
HP-30
HP-43
HP-34
HP-37
HP-32
HP-33
HP-31
HP-5
AH-7
210
206
203
7
13
HP-35
HP-29
HP-39
HP-38
HP-36
HP-42

Figure 5-19: BTEX Concentrations (µg/L), from November 1999 Sampling, Zero Contour From Mullick 1999, C.I. = Irregular

6.0 DISCUSSION

6.1 ASSESSMENT OF FIELD RESULTS

6.1.1 Contaminant Assessment

6.1.1.1 Groundwater Contaminant Assessment

The main contaminants of concern at the Cold Lake landfill are TCA, DCA, and BTEX. The concentrations of these contaminants were examined and the measured concentrations are listed in Table 5-6. Figures 5-17, 5-18, and 5-19 show the contaminant isopleths for TCA, and DCA and BTEX. The isopleths are based on the November 1999 sampling program. The non-detect boundary on the sides of the plumes are based on the 1998 sampling program (Mullick, 1999). The isopleths in Figure 5-17 and 5-18 showed that there was an increase of DCA downstream of the presumed source of TCA at well 27. This increase in DCA, a microbial metabolic by-product of TCA degradation, indicates that biodegradation was likely occurring while the TCA plume was moving downstream.

The concentration of TCA (Figure 5-17) ranged from non detect to 11 000 µg/L, the highest concentrations occurring at HP-34 and well 27. The DCA concentrations ranged from non-detect to 2400 µg/L, the highest concentrations at well 27 and well 205, slightly downstream from well 27. The DCA plume extends further downstream, away from the source, than the TCA plume.

There is good agreement between the duplicates for Well 27, HP-28, and HP-39.

Furthermore, for all the rinsate and field blanks, there were non-detectable levels of all contaminants, which indicated good field quality control.

The Canadian Council of Ministers of the Environment (CCME) interim assessment criteria guidelines for soil and water are listed in Table 5-7. There are currently no drinking water guidelines listed for chlorinated aliphatic hydrocarbons (TCA and DCA). However, the concentrations measured exceed the interim assessment criteria for water at contaminated sites, which is 0.1 µg/L. The interim guidelines are limits for contaminants in soil and water that are intended "to maintain, improve, and protect environmental quality and human health at contaminated sites". The interim assessment criteria are approximate background concentrations or approximate analytical detection limits for contaminants in soil and water (CCREM, 1991). Table 5-8 shows the CCREM remediation criteria for water for comparison with the interim assessment criteria in this report. These are values established to ensure that a remediated site effectively meets conditions in which its contaminants are no longer at risk of being exposed to receptors via groundwater transport.

Total measured BTEX values (Table 5-6 and Figure 5-19) range from non-detect to 21000 µg/L, occurring at HP-42, which is located near the original assumed source (oil pit) that was excavated in 1997. These values are much greater than the drinking water guideline of 5 µg/L, and the interim assessment criteria of 0.5 µg/L, for each compound, shown in Tables 5-7 and 5-8. The BTEX plume extends beyond HP-41, the furthest downgradient sampling point, so there is insufficient information to determine the non-detect boundary on the northeast end of the plume. Thus, it is difficult to determine whether the BTEX plume extends into the bog. The BTEX plume appears to extend beyond the TCA plume, which would be beneficial for TCA microbial mineralization. BTEX or some other substrate is required as an electron donor for degradation of TCA (the electron acceptor).

All the individual contaminant concentrations were well below the solubility limits of the compounds, listed in Table 5-9, and free product was not expected to be present near the water table. This is corroborated by the absence of free product when the wells were measured with a water level/free product indicator. The one exception was in October, 1999, when approximately 0.01 m free product was found in Well 7 and free product had previously been detected in the well in August, 1997 and June, 1998. The free product was sampled and sent for analysis, to Norwest Laboratories, in December, 1999. The free product was found to contain light hydrocarbons ranging from C7 to C16 with some traces of C18 to C32 hydrocarbons, suggesting possible lubricating material. The periodic appearance of free product in Well 7 is in conflict with the overall trends in measured dissolved contaminant in the groundwater and therefore should be monitored carefully in the future.

6.1.1.2 Soil Contaminant Assessment

Soil samples were taken from adjacent to Well N and Well 27 and the results of the analysis are shown in Table 5-10. The samples from Well N were taken at two depth intervals. The first was at approximately 0.5 m below the ground, approximately 1 m above the groundwater table or near the middle of the sand layer. The second was at approximately 3 m below ground level, approximately 0.5 m below the groundwater table. Measured contaminant concentration in the first sample were 113 000 μg/kg

BTEX, 29 000 µg/kg TCA, and < 1000 µg/kg DCA. Measured contaminant concentrations in the sample below the groundwater table were 1970 µg/kg BTEX, 450 µg/kg TCA, and 58 µg/kg DCA. The concentration of BTEX and TCA in the vadose zone are much higher than those below the groundwater table. Both the BTEX and TCA values exceed the interim assessment criteria for soil (Table 5-7). It was suspected that the locations were the original sources and that the groundwater had since transported the dissolved contaminants downstream. The very low to non-detectable concentration of DCA in the vadose zone supports the supposition that DCA is not a parent compound. TCA biodegradation to DCA would not be expected to be significant in the aerobic vadose zone, so DCA in the groundwater is likely only due to in-situ anaerobic biodegradation of TCA.

The samples around Well 27 were taken at three locations: two metres upgradient (southwest), 10 to 15 metres downgradient (northeast), and one metre crossgradient (northwest) of Well 27. For each location, three soil samples were taken: at the top (above the groundwater table), middle (at the groundwater table) and base (below the groundwater table and near the till interface) of the sand layer. Concentrations of CAH were found to decrease with depth. BTEX was also found to decrease with depth. BTEX at the top of the sand layer values ranged from 22 800 µg/kg (crossgradient, adjacent to Well 27) to 54 000 µg/kg (downgradient), and at the bottom of the sand layer near the till from 179 µg/kg (downgradient) to 615 µg/kg (adjacent to Well 27). 1,1,1-TCA values at the top of the sand layer ranged from 3400 µg/kg to 6100 µg/kg and at the bottom of the sand layer from 120 µg/kg to 520 µg/kg. DCA values at the top of the sand layer ranged from non-detectable to 240 µg/kg and at the bottom of the sand layer from 30 µg/kg to 130 µg/kg. The contamination seems to be moving in the direction of groundwater flow since the samples adjacent to Well 27 (in the northwest direction) contained significantly less contaminants and the contaminant concentrations downgradient from Well 27 were similar to those found upgradient of Well 27. This assessment appear to confirm the preliminary findings of the Mullick 1999 study, that there is a second source of TCA in the vicinity of Well 27.

6.1.1.3 Assessment of Contaminant and Geochemical Indicators

Based on the measurements of Fe^{2+} from Mullick (1999) and from this study (Figure 5-5), iron reduction appears to be ongoing as far downgradient as HP23, Well 16 and possibly HP-14. In the study recently completed, small amounts of methane (Figure 5-6) were observed at HP-40 and 41, and significant amounts were observed at well 206. These measurements indicate that methanogenesis is occurring well downgradient of the source, though not as far as iron reduction. When these results are superimposed on the measured TCA plume (Figure 5-17), it appears that the entire plume is in a reducing environment. Reductive dechlorination proceeds very well in methanogenic zones, and the literature suggests that it is also very efficient in iron and sulfate reducing zones (Kennedy et al., 1999). The downgradient extent of the BTEX plume extends beyond the TCA plume, so there is expected to be adequate amounts of electron donor (substrate) to support reductive dechlorination as well. Given the above, the conditions appear to be conducive for the TCA to be reduced to DCA in the subsurface. If the TCA plume extended beyond the highly reduced zone or the BTEX plume, reductive dechlorination would be less likely depending on if there were other substrate sources in the vicinity. The low concentrations of TCA measured in the surface water of the bog from the RRMC study (Table 4-1, SW2) indicated that TCA may have been emanating in the surface water at the ppb (µg/L) level, but their results were not corroborated in the

Mullick (1999) study. Thus it is believed that the bulk and possibly all of the TCA is being microbially mineralized below detectable levels before it is coming in contact with surface water at the bog. It has not been observed in storm water drain effluent, and all measurements indicate that the plume does not intersect the drain line.

The DCA plume extends beyond the downgradient extent of sampling (Figure 5-18). Sampling was not done further downgradient due to extreme difficulty of access due to the presence of the bog and treed areas. Since DCA can be microbially mineralized aerobically, it is expected that within the bog, where the groundwater emanates, the DCA will be readily mineralized and/or sorbed. The extent of the two processes cannot be quantified in the current study. Based on surface water measurements in the RRMC study, very low but detectable concentrations (Table 4-1, SW3) were observed in surface water in 1991. However, Mullick (1999) did not detect it in surface water measurements.

An accumulation of vinyl chloride (VC) may be expected to be produced from the degradation of TCA and DCA. However, vinyl chloride concentrations were non-detectable in all the groundwater samples. As previously mentioned VC dechlorinates into ethene and then to carbon dioxide under aerobic or anaerobic conditions. VC is difficult to sample since it is highly volatile. Furthermore, it is possible that, on the site, it transforms into ethene at an equal or higher rate than TCA and DCA degradation produce it.

The BTEX plume extends beyond the downgradient extent of sampling (Figure 5-19). Sampling was not done further downgradient due to extreme difficulty of access due to the presence of the bog and treed areas. As with the DCA, BTEX can be microbially mineralized aerobically much faster than anaerobically, so it is expected that within the bog, where the groundwater emanates, the BTEX will be readily mineralized and sorbed. The extent of the two processes cannot be quantified in the current study. No BTEX was detected in the surface water samples in the Mullick (1999) study.

Based on the above, it appears that the risk to receptors from the measured plumes is low to very low providing the land use does not change. The plume has likely reached steady state given that it is in excess of 40 years old. It may be decreasing in size, but inadequate data over time are available to confirm this. Given that retarded groundwater velocities are in the order of 20-40 m/yr, the plume is not expected to be expanding, though groundwater modeling should be conducted to enhance understanding of the behavior.

Source removal is an option, but given the nature of the landfill the source may be elusive. Though there appears to be a second source of TCA in the vicinity of well 27, its vertical and lateral extent are not well defined. There may also be other smaller sources scattered throughout the landfill that have not been identified.

6.2 DISCUSSION OF LABORATORY MICROCOSM TEST RESULTS

6.2.1 Trends Observed in Microcosm Tests

There were no particular trends to be deduced from the graphs of concentration versus time for both sites (Well N and Well 27) and both temperatures (10°C and 20°C). Due to the large variation in the data, it was suspected that some errors occurred as a result of the methodology used. Some postulated errors that may have caused this variability were reviewed during the experiment. They include: the analysis was being performed with concentrations outside the linear part of the calibration curve, the dilution factor was too large, there were volatile losses during dilution from mixing with a volumetric flask, or there were variations between vials and too few samples taken from each sample vial. These are addressed individually below.

To check these methods, the calibration, which was completed before the microcosm tests started, in October, 2000, several more data points were added in February and March. The points added on each date are indicated in Table C-2 in Appendix C. Initially, only concentrations of standards ranging from 10 μg/L to 200 μg/L were included in the calibration curve. However, in March, standards with a concentration of 1 μg/L were added to the curve. Furthermore, additional standards at 10, 30, 50, 100, and 200 μg/L were analysed to check if there was still close correlation with the existing calibration points on the curve. As a result, the regression was improved and the coefficients were found to range between 0.98 to 0.99 for all compounds.

The dilution procedure prior to GC injection was changed from using the volumetric flask to using a 5 mL gas tight syringe instead on February 20, 2001. The new dilution involved diluting 40 μL of supernatant into the 5 mL of deionized water and using the same syringe to inject the whole sample into the purge and trap. During dilution, there was a possibility of differences in the resulting concentration since one could not obtain exactly 40 μL every time. Performing the dilution with ± 5 μL would result in a ± 100 μg/L change in concentration. The change in this method did not seem to affect the results, indicating that there had been minimal volatile loss by using the volumetric flask for mixing.

Finally, to check the repeatability of sampling from the same vial, triplicate samples were taken from each of the three replicate microcosm vials on February 6 and 7, 2001. A 600 μL aliquot of supernatant from a given microcosm vial was drawn, and three 200 μL aliquots were deposited into each of three 25 mL volumetric flasks and mixed. From each volumetric flask, 5 mL of solution was drawn and analyzed in the GC. The results of the triplicate testing showed that the absolute value of concentration deviation measured in the larger sample set (9) was similar to that of the smaller sample set (3).

The lowest detectable concentrations for each contaminant were determined for each compound, from the GC calibration. It appears that the DCB's were mostly non-detect, but some 1,2-DCB and 1,3-DCB results were sporadic. The reason for the sporadic nature may be that the microcosm supernatant contains other compounds that elute at around the same times, causing a buildup of contaminants at the same retention time that 1,2-DCB is detected.

The concentrations observed in the negative controls were fluctuating to an extent that the presence or absence of abiotic degradation processes could not be determined. On some of the negative control vials the Teflon liner glued to the butyl rubber septa became detached. These negative controls had lower concentrations of TCA and DCA than the other ones suggesting volatile loss/sorption to the septa may have occurred.

Another possible explanation for the high variation in both the negative controls and the regularly sacrificed samples was that each microcosm was different. The microcosms were prepared as uniformly as possible but there were still physical and chemical differences between the individual microcosms. The diversity among the individual microcosms coupled with the deviation in the sampling technique may have played a part in the variation in the data but the magnitude of effect on the results due to these errors cannot be quantified. Some of the microcosms may have contained soil with small amounts of free product (such as Well N). In these microcosms, the concentrations would have increased over time, exceeding the originally expected concentrations because the TCA free product partitioned into the supernatant over time. Since the concentrations of TCA in the supernatant are less than the solubility of TCA, such partitioning is highly possible, especially at the higher temperature since the process would reach equilibrium more quickly at higher temperatures. If the experiment could be repeated, each microcosm would need to be prepared more carefully, ensuring soil and water homogeneity, or in-situ microcosms would be used instead.

The laboratory experiments required collection, transport, storage, and handling of aquifer samples (groundwater and/or aquifer sediment) that may have affected parameters such as pH, Eh, dissolved oxygen, and temperature. In addition, the laboratory experiments were performed at a much higher groundwater to sediment ratio than found in the field and certain chemical changes may have occurred during the experiment. Redox conditions were not measured in these microcosms; however, for further studies, it may be helpful to measure the conditions at the start and finish of the microcosms.

Finally anaerobic rates are very slow, so studies may have to be conducted with durations of one year to 18 months. The residence time of a plume may be several years to tens of years at field scale. Thus rates of transformation that are slow in terms of laboratory experimentation may have a considerable environmental significance. A microcosm study lasting only a few weeks to months may not have the resolution to detect slow changes that are of environmental significance (Weidemeier et al., 1998).

Microcosm tests can measure the rate of change of the constituents of concern as well as changes in pH and microbial populations (Norris, 1994). Since the microcosms in the 10°C incubator had been frozen (at -10°C) for an unknown length of time, a maximum of two days, their properties may have changed so that they could no longer biodegrade the contaminants in the microcosm vials. The samples were frozen before the December 12, 2001 sampling event. The rate of storage death of bacteria is much greater at 0 to -10°C than at lower temperatures. The permeability of the bacterial cell increases if bacteria are suddenly frozen and subsequently thawed. Low molecular weight intracellular solutes such as nucleotides and amino acids are released and other compounds are more readily absorbed. Results in samples that were frozen before testing are likely not to be representative of the material at the time of sampling (Mitscherlich, E., 1984). If the microorganisms were in a state of slow growth, the sudden shock in change of temperature would not affect them for long. However, if they were in a state of fast growth. the change would make a large difference (Gaudy and Gaudy, 1980). Additionally, the storage time of the soil and groundwater samples, of approximately two and a half months, could have been a factor in the variations of the microcosm tests. Over time, the volatiles could have stripped from the batches of soil, the soil contamination could have settled so that upon mixing the soil into the individual microcosms, some microcosm vials may have received more highly contaminated soil or groundwater, thereby causing the variations in the microcosms.

7.0 CONCLUSIONS AND RECOMMENDATIONS

1. Intrinsic bioremediation is believed to be ongoing for all contaminants of concern evaluated at the site based upon:

- Decreased contaminant concentration downgradient of the source;
- Changes in electron acceptor concentrations across the site; and
- Observed increase in daughter products of TCA reductive dechlorination (DCA) downgradient of TCA source.

2. TCA concentrations appear to be decreasing to below detection limits upgradient of the bog.

3. Very low (µg/L) levels of TCA were observed in and beyond the bog in 1991, but none was detected in those areas in 1999.

4. DCA and BTEX are at elevated concentrations beyond the upgradient edge of the bog. DCA was observed at very low concentrations (µg/L) in and beyond the bog in 1991 but not in 1999. Since these contaminants can be degraded aerobically, migration beyond the bog is not anticipated. They will likely be microbially

mineralized or sorbed before they will pose a threat to receptors.

5. Removal of the second source will be difficult given the nature of the landfill and the uncertainty of what was buried and where it was buried.

6. Containment of the plume is a possible option but since the risk to receptors is low to very low, providing land use does not change, it is likely unnecessary. This may have to be addressed with the regulators.

Based upon the above, it is recommended that continued monitoring of the site be implemented. Source removal is not recommended at this time since the location of the source(s) is not well defined, and the impact (reduction) of contaminant transport is likely to be marginal. If it is decided that no contaminants are to be allowed to enter the bog area, an interception and treatment strategy is likely the most effective (though still costly) solution.

Monitoring of the plume should be implemented as a risk management strategy. If it is necessary to locate the downgradient extent of the BTEX and DCA plumes, a further sampling program will be necessary. It will, however, be very difficult (and expensive) given the terrain. Winter installation of monitoring wells may be necessary.

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APPENDIX A

ENVIRO-TEST LABORATORY METHODOLOGY

Appendix A Test Methodologies

Balance Laboratory Code: BAL
Instrumental Method:Sum(Anions)/Sum(Cations)*100
Method Reference: APHA 1030 F

Bicarbonate (HCO3) Laboratory Code: BIC1W1
Instrumental Method: Calculated from Alkalinity
Method Reference: APHA 2320B

Chloride (Cl) Laboratory Code: CHL1W1
Preparation: Filter through 0.45u filter
Instrumental: Sample analyzed colorimetrically @ 480 nm using ferricyanide method on a Cobas Fara discrete analyzer
Reference: APHA 4500-Cl, E

or

Preparation Method: 0.45μ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B

Carbonate (CO3) Laboratory Code: CO31W1
Instrumental Method: Calculated from Alkalinity
Method Reference: Carbonate APHA 2320B

Conductance (EC) Laboratory Code: ECW1W1
Instrumental Method: Conductivity Meter
Method Reference: Conductance APHA 2510B

Iron, Extractable Laboratory Code: FEE2W1
Preparation Method: 0.45u Filtration
Instrumental Method: Atomic Absorption Spectroscopy - flame
Method Reference: APHA 3500 B

Fluoride Laboratory Code: FLO1W1
Preparation: Requires addition of TISAB buffer
Instrumentation: Ion selective electrode
Reference: APHA 4500-F,C

Hardness Laboratory Code: HARD
Instrumental Method: Calculated from Ca+Mg as CaCO3
Method Reference: Hardness APHA 2340 B

ICP Metals Setup Laboratory Code: ICPDIS
PREPARATION METHOD:

Dissolved:	Filter through 0.45u and preserve with nitric acid
Extractable:	Preserve with nitric acid
Total:	Preserve with nitric acid; digest with nitric/hydrochloric acid

INSTRUMENTAL METHOD: ICP Spectrophotometry
METHOD REFERENCE: APHA 3120B/3030F, Standard Methods; 18th ed.

Routine Metals Laboratory Code: ICPRDS
PREPARATION METHOD: Filter through 0.45u and preserve with nitric acid
INSTRUMENTAL METHOD: ICP Spectrophotometry
METHOD REFERENCE: APHA 3120B/3030F, Standard Methods; 18th ed.

Sulfur reported as sulfate. ICP result multiplied by 3 to convert.

Appendix A Test Methodologies

Sulfate (SO4) Laboratory Code: ICPSO4

Preparation Method: 0.45 u filtraton if turbid
Instrumental Method: Ion Chromatography or ICP
Method Reference: S04 Dionex Handbook of Ion Chromatography pg 37.

Manganese, Extractable Laboratory Code: MNE2W1

Preparation Method: 0.45u Filtration
Instrumental Method: Atomic Absorption Spectroscopy - flame
Method Reference: APHA 3500 B

Nitrate+Nitrite (N) Laboratory Code: N231W1

Preparation Method: 0.45µ Filtration
Instrumental Method: Automated colorimetry (Cobas Fara Discrete analyzer)
Hydrazine reduction @ 520 nm
Method Reference: APHA 4500-NO3-H

or

Preparation Method: 0.45µ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B
and
Preparation Method: 0.45µ filtration if turbid
Instrumental Method: Ion Chromatography
Method Reference: APHA 4110 B

Hydroxide Laboratory Code: OHX1W1

Method Reference: Hydroxide APHA 2320 B
Instrumental Method: Calculated from Alkalinity

pH in Water Laboratory Code: PHW1W1

Instrumental Method: pH Meter
Method Reference: APHA 4500-H+ B

Total Alkalinity Laboratory Code: TAL2W1

Instrumental Method: If pH<8.3 on the initial sample, titration for alkalinity will be performed to pH 8.3 and 4.5 endpoint, using autotitrator or manual technique.

Method Reference: T ALK APHA 2320B

TDS (Calculated) Laboratory Code: TDS

Instrumental Method: Calculated from the sum of ions
Method Reference: TDS APHA 1030 F

Total Organic Carbon Laboratory Code: TOC1W1

Instrumental Method: Combustion - Infrared carbon analyzer
Method Reference: TOC APHA 5310 B

Turbidity Laboratory Code: TUR1W1

Instrumental Method: Nephelometer
Method Reference: Turb APHA 2130B

Volatile Organics (MS):H20 Laboratory Code: VOC1W1

Preparation Method: Automated headspace

Instrument Method: GC/MS analysis

Appendix A Test Methodologies

Method Reference: Extraction Method: EPA 5021 (modified)
Analytical Method: EPA 8240 (modified)

Interferences: *** Values for 1,1,2,2-tetrachloroethane and trichloroethene may not accurately reflect concentrations present in the sample(s) due to the decomposition of the former to the latter when exposed to heat and pressure. (See MOEE Method PETHC-E3132A, 1.5.1.5 Dehydrohalogenation)

Key To Sub-Contracted Laboratory Identification:

Laboratory	Test Code # *	Laboratory	Test Code#
ETL - Edmonton	1,5	Core Laboratories	C
ETL - Calgary	2	HydroQual	H
ETL -Saskatoon	3	SRC	R
ETL - Thunder Bay	7	Biochem	B
ETL - Winnipeg	8	Bioquest	Q
ETL - Grande Prairie	9	WSH Laboratories	W
ETL - Mobile Services	L	Maxxam	M
Bodycote	E	Alpha Laboratories	A
Norwest Laboratories	N		

* The Test code #/Letter is the last character on the test code.
For Example: NMA1W3 designates that the test was performed in the ETL Saskatoon laboratory.
THIS IS THE LAST PAGE OF THE METHODOLOGY APPENDIX.

APPENDIX B

METHANE CALCULATIONS AND INSTRUMENT SPECIFICATIONS

Gas Chromatography specifications for Methane Analysis

HP 5700, Flame Ionization Detector

Detector Temperature: 250°C

Oven Temperature: 35°C

Injection Temperature: 0°C

Ambient Temperature: 26°C

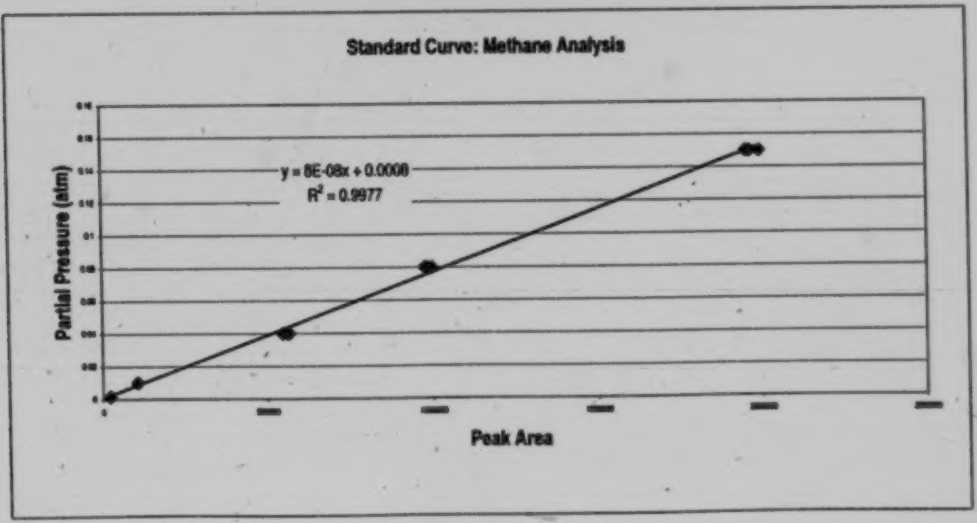
Column: Tenex GC, 60/80 Resin Mesh, Uncoated 6' Long

Flow Rates:	Helium	35mL/min
	Air	327 mL/min
	Nitrogen	49.5 mL/min

METHANE STANDARD CURVE November, 1999 Sampling

Temperature (deg C):	25	
Henry's Constant (atm*L/mol):	13.411 x 10^{-4}	
ρ CH_4 (g/L):	0.7174	
MW (g/moL)	16.04	
mol air:	0.005711	
Assume STP	1 atm	0 deg C

% CH_4	VOL INJECTED (mL)	PEAK AREA	MOLE METHANE (mol)	MOLE FRACTION (x_g)	PARTIAL PRESSURE
0.16	0.00025	22142	1.11814E-08	1.66622E-06	0.0016
0.16	0.00025	21779	1.11814E-08	1.66622E-06	0.0016
0.16	0.00025	21478	1.11814E-08	1.66622E-06	0.0016
1	0.0016	104284	7.15611E-08	1.06638E-05	0.01
1	0.0016	103558	7.15611E-08	1.06638E-05	0.01
1	0.0016	102956	7.15611E-08	1.06638E-05	0.01
4	0.0066	565410	2.9519E-07	4.39883E-05	0.04
4	0.0066	546050	2.9519E-07	4.39883E-05	0.04
4	0.0066	562430	2.9519E-07	4.39883E-05	0.04
8	0.01374	982370	6.14531E-07	9.15757E-05	0.08
8	0.01374	996860	6.14531E-07	9.15757E-05	0.08
8	0.01374	976420	6.14531E-07	9.15757E-05	0.08
15	0.0279	1964740	1.24785E-06	0.000185951	0.15
15	0.0279	1993720	1.24785E-06	0.000185951	0.15
15	0.0279	1952840	1.24785E-06	0.000185951	0.15



METHANE ANALYSIS: November, 1999

Temperature: 25 deg C
Molecular weight 16 g/mol
Headspace Volume (Vg 4 ml
Liquid Volume (Vw) 39.8 ml

Henry's Constant 41300 unitless

Temperature: 25 deg C

$$C=MW\left[\frac{55.5}{H}+\frac{V_g}{V_w}\frac{1}{22.4}\frac{273}{(T+273)}\right]X_g$$

WELL SITE	REP #	PEAK AREA	PARTIAL PRESSURE y=8E-8x+0.0008	Groundwater Concentration (mg/L)	AVERAGE TOTAL CONCENTRATION (mg/L)
AH-7	1	220810	0.01847	1.612	1.62
	2	219610	0.01838	1.604	
	3	225960	0.01888	1.647	
HP-41-2	1	19026	0.00232	0.203	0.20
	2	18825	0.00231	0.201	
	3	19526	0.00236	0.205	
HP-45	1	176440	0.01492	1.302	1.31
	2	179920	0.01519	1.326	
	3	177580	0.01501	1.310	
Well 27-2	1	37877	0.00384	0.335	0.34
	2	38026	0.00384	0.335	
	3	39296	0.00394	0.344	
HP-38	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-40-2	1	38214	0.00386	0.337	0.33
	2	37424	0.00379	0.331	
	3	37208	0.00378	0.330	
HP-39-2	1	52981	0.00504	0.440	0.44
	2	53162	0.00505	0.441	
	3	50611	0.00485	0.425	
R3	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
211	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-36-2	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-38-2	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-31-2	1	103280	0.00906	0.791	0.78
	2	101480	0.00892	0.778	
	3	100770	0.00886	0.773	
HP-37	1	60679	0.00565	0.493	0.49
	2	61560	0.00572	0.500	
	3	59171	0.00553	0.483	
HP-43	1	213480	0.01788	1.560	1.64
	2	212300	0.01778	1.552	
	3	249660	0.02077	1.812	
HP-34	1	396730	0.03254	2.840	2.76
	2	377750	0.03102	2.707	
	3	383680	0.03150	2.748	
HP-44	1	107670	0.00941	0.821	0.81
	2	104870	0.00919	0.802	
	3	104610	0.00917	0.800	
R2	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
Well N-2	1	130560	0.01124	0.981	0.96
	2	131130	0.01129	0.985	
	3	122850	0.01063	0.927	
Well N	1	184480	0.01556	1.358	1.36
	2	182540	0.01540	1.344	
	3	187140	0.01577	1.376	
Well 205-2	1	226980	0.01894	1.652	1.43
	2	231500	0.01936	1.689	
	3	126050	0.01088	0.949	
F3	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-27	1	71535	0.00652	0.569	0.59
	2	74784	0.00678	0.592	
	3	75876	0.00687	0.600	
HP-29	1	175830	0.01487	1.298	1.29
	2	171580	0.01453	1.268	
	3	175180	0.01481	1.293	
HP-30	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-28-2	1	195880	0.01647	1.437	1.42
	2	192600	0.01621	1.414	
	3	192250	0.01618	1.412	
HP-33-2	1	18929	0.00231	0.202	0.20
	2	19590	0.00237	0.207	
	3	18724	0.00230	0.201	
F2	1	0	0.00080	0.070	0.07
HP-42-2	1	19746	0.00238	0.208	0.21
	2	20193	0.00242	0.211	
	3	20019	0.00240	0.210	
HP-35	1	688480	0.05588	4.876	4.92
	2	701000	0.05688	4.964	

HP-32	1	200040	0.01685	1.471	1.46
	2	194810	0.01638	1.428	
	3	197560	0.01660	1.449	
HP-43-2	1	220060	0.01840	1.613	1.59
	2	216960	0.01816	1.594	
	3	217260	0.01816	1.587	
HP-44-2	1	93985	0.00825	0.729	0.72
	2	94654	0.00837	0.731	
	3	91570	0.00813	0.709	
HP-27-2	1	75163	0.00681	0.595	0.54
	2	50326	0.00483	0.421	
	3	73240	0.00667	0.582	
	4	71812	0.00655	0.572	
HP-30-2	1	0	0.00080	0.070	0.07
HP-42	1	24558	0.00270	0.241	0.25
	2	25994	0.00287	0.251	
	3	25615	0.00284	0.248	
	4	25354	0.00283	0.247	
HP-31	1	99898	0.00880	0.768	0.78
	2	102770	0.00882	0.767	
	3	103850	0.00910	0.794	
HP-38	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-35-2	1	230230	0.01922	1.677	1.68
	2	232280	0.01938	1.691	
	3	229230	0.01914	1.670	
HP-33	1	16761	0.00230	0.201	0.20
	1	18831	0.00231	0.201	
	1	18511	0.00228	0.199	
HP-34-2	1	305770	0.02536	2.204	2.21
	2	306800	0.02540	2.224	
	3	305110	0.02521	2.200	
HP-32-2	1	140880	0.01205	1.054	1.04
	2	128870	0.01112	0.970	
	3	149870	0.01246	1.088	
R1	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-40	1	44265	0.00434	0.379	0.38
	2	43061	0.00424	0.370	
	3	44311	0.00434	0.379	
R4	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
HP-41	1	21381	0.00251	0.219	0.23
	2	23167	0.00265	0.232	
	3	22713	0.00262	0.229	
	4	23867	0.00269	0.234	
HP-37-2	1	37111	0.00377	0.329	0.33
	2	34986	0.00356	0.311	
	3	37464	0.00380	0.331	
	4	37482	0.00380	0.331	
HP-29-2	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
F4	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
AH-7-2	1	242210	0.02016	1.761	1.75
	2	240340	0.02003	1.749	
	3	238910	0.01990	1.745	
Well 205	1	228370	0.01907	1.664	1.67
	2	226100	0.01889	1.648	
	3	231910	0.01935	1.690	
HP-45-2	1	259620	0.02133	1.861	1.84
	2	251070	0.02089	1.823	
	3	254500	0.02118	1.847	
HP-36	1	28474	0.00292	0.256	0.26
	1	28880	0.00295	0.257	
	1	28346	0.00307	0.268	
Well 211-2	1	0	0.00080	0.070	0.07
	2	0	0.00080	0.070	
	3	0	0.00080	0.070	
Well 27	1	55150	0.00521	0.465	0.45
	2	56291	0.00522	0.456	
	3	53013	0.00504	0.440	

APPENDIX C

GAS CHROMATOGRAPHY CALIBRATION AND ANALYSIS PROCEDURES

C.1 Preparation of chemical solutions for Gas chromatography

All stock solutions were created from neat solution provided by Sigma-Aldrich Laboratories. The neat solutions were diluted to the desired concentrations for each stock solution. All solution handling was done under a fume hood in the Newton building Analytical Chemistry Laboratory. After each stock solution was prepared it was refridgerated in the freezer below 0°C. Diluted stock solutions were placed in the refridgerator at 4°C.

Materials

- 10 mL volumetric flask
- 500 mL volumetric flask
- flask stoppers
- sealing tape
- syringes
- pipette
- fume hood
- methanol
- deionized water
- neat solutions of 1,1,1-TCA, DCA, 1,2-DCB, 1,3-DCB, 1,4-DCB, fluorobenzene (the surrogate standard), and
  1, Bromo-2, Chloropropane (internal standard)

C.1.1 Individual stock solutions

Individual stock solutions were made of all the compounds of interest: 1,1,1-TCA, 1,1-DCA, 1,2-DCB, 1,3-DCB, 1,4-DCB, and fluorobenzene (the surrogate standard). Using a 10 mL volumetric flask, the flask and the stopper were weighed on a scale. After weighing the flask and stopper, 10 drops of neat solution were added into the flask and the stopper was placed back on. It is crucial to place the stopper back onto the flask to reduce volatilization of the solution. The flask, solution, and stopper are then re-weighed and we take the weight difference to get the weight of the 10 drops of neat solution. 10 drops of neat solution are roughly equivalent to 10 mL of the solution. Therefore, the concentration would be the mass of the solution per 10 mL of solution. For example, if the weight of the 10 drops is 0.0991 g, the solution concentration would be 99.1 mg/10 mL or 9.91 mg/mL.

Creating an individual secondary stock solution in methanol

The next step is to create a secondary stock solution. A solution of 1 mg/mL in 10 mL methanol can be made by determining how much stock solution to place into the 10 mL of methanol to create the new solution. If 10 mg/10mL is required, the calculation is as follows:

$C_1V_1 = C_2V_2$

$(9.91 \text{mg/mL})(x \text{ mL}) = (1 \text{mg/mL})(10 \text{mL})$

$$x\ \text{mL} = \frac{(1\text{mg/mL})(10\text{mL})}{9.91\ \text{mg/mL}} = 1.13\ \text{mL} = 1.2\ \text{mL}$$

Then add 1.2 mL of the stock solution into 10 mL of methanol.

Creating a further diluted individual secondary stock solution in water

A final solution of each individual stock solution in methanol is made so that it can be tested through the purge and trap and gas chromatography to make a standard curve. If the target is to create a 500 μg/L solution in water, this is about 500 μg/L or 0.5 mg/L in dilute solutions. To make a solution in 500 mL of water, the amount of individual secondary stock solution in methanol to add can be determined by the following calculation:

$$C_1V_1 = C_2V_2$$

$$(1\text{mg/mL})(x\ \text{mL}) = (0.5\text{mg/L})(500\text{mL})$$

$$x\ \text{mL} = \frac{(0.5\ \text{mg/L})(1\text{L}/1000\text{mL})(500\text{mL})}{(1\text{mg/mL})} = 0.25\ \text{mL}$$

Therefore 0.25 mL of the individual secondary stock solution in methanol must be added to 500 mL of water to create the 500ppb solution.

C.1.2 Secondary standard solution (a combination of all individual secondary stock solutions)

To create a complete standard with all the individual secondary stock solutions for fast analysis through the purge and trap and gas chromatography, the individual secondary stock solutions in methanol are used. Each solution is added into a 500 mL volumetric flask to create a new secondary standard with a concentration of about 500ppb.

For example, if 1,1,1-TCA had a concentration of 9.91 mg/mL, approximately 1.0 mL of individual stock solution would be added into 10 mL methanol to create a new 1 mg/mL solution. For a concentration of 1 mg/mL in 25 mL methanol, about 2.5 mL of individual stock solution would be added. Since it is difficult to measure the exact volume of solution (because they are small quantities), the separate volumes are rounded to the nearest tenth of a decimal and a "real" concentration is calculated for each in 25 mL methanol. All will be close to 1mg/mL. The following calculation is used:

$$C_1V_1 = C_2V_2$$

$$(\text{about } 1\ \text{mg/mL})(x\ \text{mL}) = (500\ \mu\text{g/L})(500\ \text{mL})$$

This 25 mL size in methanol is used for storing the secondary standard in the freezer so that it lasts for a few months.

The desirable final concentration is 500 µg/L in 500 mL of water so the volume of each individual stock solution to add into the 500 mL of water must be determined.

$$X\text{ mL} = \frac{(0.5\text{ mg/L})(1\text{L}/1000\text{ mL})(500\text{ mL})}{(\text{about }1\text{ mg/mL})} = 0.255\text{ mL}$$

A volume for every compound in the list will be obtained, including the surrogate standard.

The actual concentration of the secondary standard can then be back-calculated by taking an average of all the volumes of each stock solution added. In this case, the average volume of each stock solution added was 0.25 mL.

$$C_1V_1 = C_2V_2$$

$$(1\text{ mg/mL})(V_{ave} = 0.25\text{ mL}) = (x\text{ mg/mL})(500\text{ mL})$$

$$x\text{ mg/mL or }C_2 = \frac{(1\text{ mg/mL})(0.25\text{ mL})}{(500\text{ mL})} = 0.000502\text{ mg/mL}$$

$$C_2 = 0.000502\text{ mg/mL} = 502\ \mu\text{g/L}$$

This new secondary standard can be stored in the refrigerator at 4°C for only a few weeks with minimal headspace.

C.1.3 Surrogate standard and the internal standard

The surrogate standard, fluorobenzene is added into a test solution during mixing of the solution, and it is to check recovery of the sample and to check resolution of the peaks while it is going through the purge and trap and gas chromatography unit. It has similar behavior to the compounds of interest.

The internal standard, 1, Bromo-2, Chloropropane, checks the analysis part, the purge of the experiment. It is used to normalize the calibration curve to account for slight differences in retention times and concentrations due to equipment errors. It shows whether the chromatogram has drifted and shows where compounds are in relation to each other. It was added into the test solution just before the purge and trap is started since the concentration always stays the same no matter what concentration of test solution is used.

C.2 Purge and Trap and Gas Chromatography

C.2.1 Description of instrumentation

The instrumentation used for chemical analysis was purge and trap and gas chromatography with a flame ionization detector (GC/FID).

The purge and trap unit first purges the sample in the sample holder. Volatilization occurs as the sample is purged and the gas moves through a line and sorbs onto the trap. Following the trapping operation, the sample is drained from the sample holder and the trap heated so that it desorbs the trapped organic material that then moves through a line to the GC.

The gas chromatographic system functions as follows: High purity helium, an inert carrier gas, flows continuously from a large gas cylinder through the injection port, the column, and the detector. The carrier gas carries the sample through the column and does not interact chemically with the sample. It provides a suitable matrix for the detector to measure the sample components. The flow rate of the gas is carefully controlled to ensure reproducible retention times and to minimize detector drift and noise. The flow rate is measured by a flow meter from time to time, for quality checks. For direct injection, the sample of interest is injected (usually with a syringe) into the heated injection port where it is vaporized and carried into the column, typically a capillary column 15 to 30 m long, coated on the inside with a thin (0.2 um) film of high boiling liquid (the stationary phase). If from purge and trap, the trapped components of the sample are desorbed from the trap and sent through a heated line to the capillary column of the GC. The sample partitions between the mobile and stationary phases and is separated into individual components based on relative solubility in the liquid phase and relative vapor pressures. After the column, the carrier gas and sample pass through a detector, in this case a flame ionization detector. This signal goes to a data system/integrator that generates a chromatogram (McNair and Miller, 1998). The integrator automatically integrates the area beneath the peak of the trace, performs calculations and prints out a report with quantitative results and retention times (McNair and Miller, 1998).

GC specifications and the parameters used

For the Purge and Trap the following program was used:

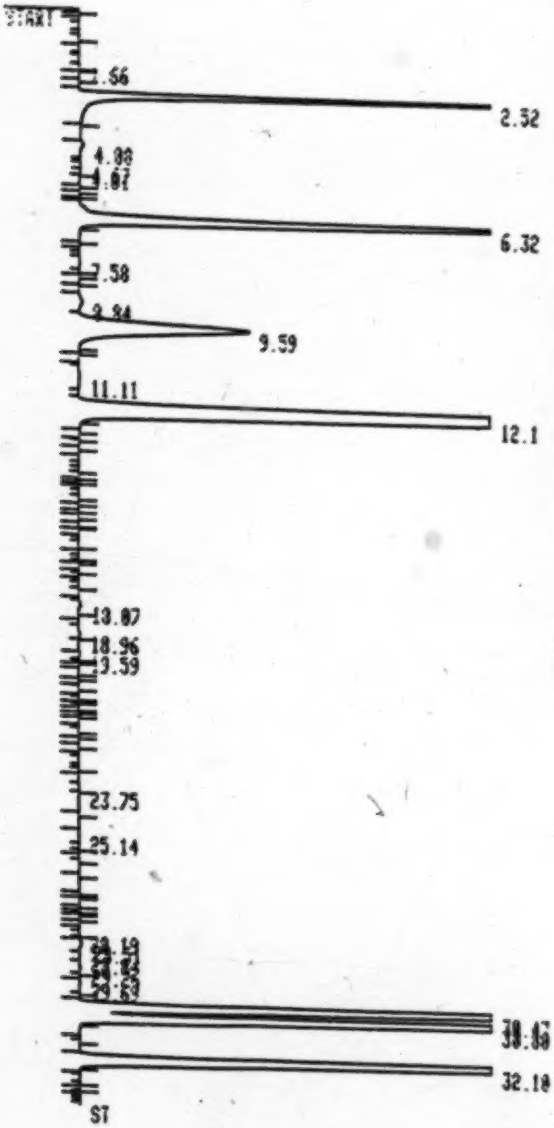
Line temperature	200°C
Valve temperature	180°C
Mount Temperature	40°C
MCS Line temperature	80°C
Purge ready Temperature	35°C
Purge Temperature	35°C
Turbo Cool Temperature	35°C
Purge Time	5 min
Dry purge time	5 min
GC start	start
GC cycle time	0
Desorb preheat	200°C
Desorb time	4 min
Desorb temperature	220°C
Sample Drain	On
Bake time	10 min
Bake temperature	225°C
BGB of Delay	0
MCS Bake temperature	225°C

The temperature program on the gas chromatograph started at 37 °C for 1 minute, increased at a rate of 4 °C /minute to 120 °C, held for 0 minutes, and then increased at a rate of 10 °C to 190 °C for 10 minutes. The bake program was 40 °C for 1 minute followed by a 32.5°C /min increase to 200 °C, held for 5 minutes.

C.2.2 GC Calibration

To get the GC calibrated and ready to analyze samples from Cold Lake, samples with known contaminant concentrations were analyzed. The five types, 1,1,1-TCA, 1,1-DCA, 1,2-DCB, 1,3-DCB, and 1,4-DCB were prepared into individual 10 mL solutions of concentration 40 μg/L. A surrogate standard, fluorobenzene, and the internal standard, 1- Bromo-2,Chloropropane, were also prepared. The seven solutions were analyzed in the GC separately and their retention times were found. For each analysis, 0.5 mL of the individual standard and 4.5 mL of deionized water were injected into the sample holder. By finding their retention times, we would be able to identify each individual standard peak from the results of the combined solution, the secondary standard. The secondary standard was made up of the five standards and the surrogate standard. The range of concentrations used to make up the calibration curve was 40ppb, 100ppb, 200ppb, 300ppb, and 400ppb. A solution of 500ppb was prepared and diluted to obtain each concentration. Once the secondary standard was diluted with distilled de-ionized water, 1/10 mL of internal standard was added to the solution and the whole mixture was run through the GC again. For each concentration there were three sample runs. Every morning, the unit would be put through a bake for about 15 minutes on the GC and for about 30 minutes for the purge and trap. After the bake, a 5 mL de-ionized water run would be put through the system to clear the system of excess organic matter on the trap and in the GC. Results were obtained from the GC and a calibration curve was generated for reference in future samples. Figure C-1 shows an example of a GC trace and Figure C-2 shows that calibration curve that was obtained for the microcosm tests.

Figure C-1: Example of a Gas Chromatograph Trace

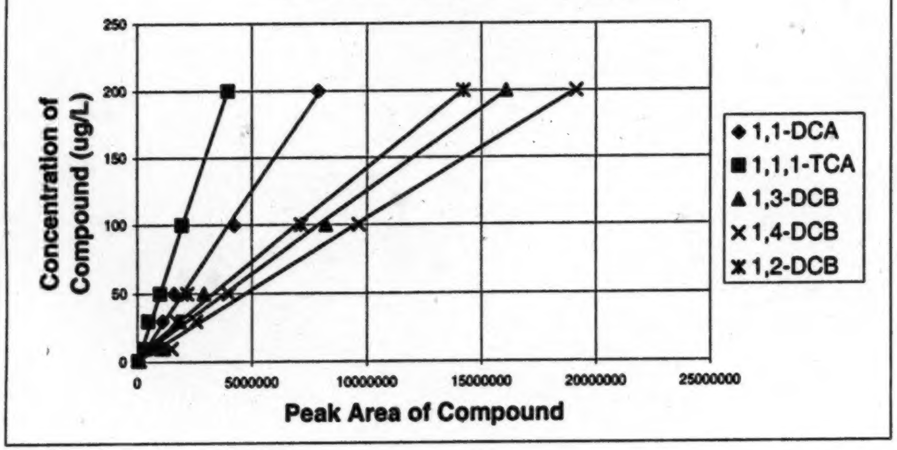


```
RUN #   47

AREA%
   RT             AREA TYPE    AR/HT        AREA%
  1.66            1044   PB    0.054        0.002
  2.52         3976200   PB    0.056        7.992
  4.08           19423   BP    0.163        0.039
  4.67            3291   VV    0.131        0.007
  4.81            4453   VP    0.120        0.009
  6.32         3328300   PB    0.179        6.690
  7.58            6812   VV    0.253        0.014
  8.84           30709   PV    0.285        0.062
  9.59         2052700   VB    0.353        4.126
 11.11           13107   PV    0.312        0.026
 12.13      1.3956E+07   PB    0.230       28.052
 18.07           14861   VB    0.159        0.030
 18.96            9956   PV    0.178        0.020
 19.59            4794   BP    0.122        0.010
 25.14            4689   PP    0.174        0.009
 28.19            1354   PV    0.135        0.003
 28.51           15951   BV    0.180        0.032
 28.84            2962   VP    0.137        0.006
 29.26            7221   PP    0.141        0.015
 29.69            6529   BP    0.176        0.013
 30.47         8643200   BV    0.136       17.373
 30.80      1.0214E+07   VB    0.136       20.529
 32.10         7434100   BB    0.158       14.942

TOTAL AREA= 4.9752E+07
MUL FACTOR= 1.0000E+00
```

Figure C-2: Calibration Curve



Compound	Equation	R^2
1,4-DCB	1e-05x+0.9289	0.9962
1,3-DCB	1e-05x+3.6132	0.992
1,2-DCB	1e-05x+4.7183	0.9876
1,1-DCA	3e-05x+0.7829	0.9943
1,1,1-TCA	5e-05x+0.0023	0.998

APPENDIX D

SORPTION AND RETARDATION CALCULATIONS

Sorption and retardation calculations

These values are calculated utilizing the total organic carbon (TOC) of the aquifer matrix and the organic carbon partitioning coefficient (k_{oc}) for each contaminant. The average TOC concentration from the most transmissive zone in the aquifer are used for retardation calculations. The k_{oc} values are calculated from:

$k_{oc} = k_d/f_{oc}$ (eq. C.1)

where k_{oc} = soil sorption coefficient normalized for total organic carbon content (L/kg);

k_d = distribution coefficient (L/kg); and

f_{oc} = fraction total organic carbon (mg organic carbon/ mg soil).

Rearranging equation C.1,

$k_d = k_{oc}f_{oc}$ (eq.C.2)

A value for f_{oc} is either determined directly in the laboratory or obtained from tables of representative values. For medium sand of glaciofluvial deposition the range is from 0.00021 - 0.019 (Domenico and Schwartz, 1990). From a study in similar sands in the 4 Wing main POL compound f_{oc} was approximately 0.007 (Thielmann, D., 1997).

Table 8-2 lists typical values of solubility, k_{ow}, k_{oc} and Henry's constants for compounds evaluated in this study.

For 1,1,1-TCA,

$f_{oc} = 0.007$,

$k_{oc} = 10^{2.18} = 151$ L/kg

Therefore, $k_d = 1.06$ L/kg

The void ratio of a saturated soil is given by

$$e = G_s w \qquad \text{(eq.C.3)}$$

where G_s = specific gravity of the soil (unitless)

w = water content (unitless or %)

For Gs = 2.65 (typical value for fine to medium sand)

and $w = 0.17$ (as determined for the site)

then $e = 0.45$.

Knowing the void ratio, the porosity may be calculated from, $n = e/(1+e) = 0.31$

The bulk density of the soil may then be calculated from:

$$\rho_b = \frac{G_s \rho_w (1+w)}{1+e} \qquad \text{(eq.C.4)}$$

$\rho_b = 2.13$ kg/L

Assuming that sorption is adequately described by the distribution coefficient (valid when $f_{oc} > 0.001$) (Weidemeier et al., 1995), the coefficient of retardation for a dissolved contaminant (for saturated flow) is given by:

$$R = 1 + \frac{\rho_b k_d}{n} \qquad \text{(eq.C.5)}$$

where R = coefficient of retardation (dimensionless)

ρ_b = bulk density of aquifer (kg/L)

k_d = distribution coefficient (L/kg)

n = porosity (unitless) = n_e

$R = 2.04$

Therefore, for this site, the retarded contaminant velocity would be $v_c = v_x/R = 40$ m/yr

APPENDIX E

MICROCOSM TEST PROCEDURE

Microcosm procedure

Listed below are the steps involved in the microcosm test preparation.

1. The samples were obtained from adjacent to two wells within the contaminated plume at the old landfill.
2. Site 1 is near Well N, which was approximately 50 m downstream from the original source (at Well 17) and was approximately 250 m upstream from Site 2. Site 2 was near Well 27, which was the presumed second source of contamination.
3. For both test temperatures (10°C and 20°C) for samples from both sites, 4 sets of tests were run with each test series consisting of 20 sampling events with 3 replicates each event. Every other sampling event contained 2 negative controls.
4. Thus a total of 2 sites x 2 temp x 20 sampling events x 3 replicates = 240 vials, plus 2 negative controls x 2 sites x 2 temp x 10 sampling events = 80 vials.
5. The 2 sterilized negative controls consist of one with groundwater only (50/50 groundwater/distilled water) and one with groundwater and soil, to account for processes other than microbial degradation.
6. Forty vials contained only water, 280 vials contained soil and water for a total of 320 vials.
7. Soil (from below the groundwater table) and water obtained from the field was refrigerated at 4 °C, to inhibit microbial degradation and volatilization during storage, for about two months, until they were used in assembly of the microcosms.
8. Microcosms were incubated at their specified temperatures (10 °C or 20 °C) until they were sacrificed. These two different temperatures were used to evaluate rates of mineralisation of TCA at different temperatures.

9. The vials were prepared under an anaerobic hood in the Biological Sciences building.
10. A mass of 15 g of soil was measured into each vial and 25 mL groundwater was added to the vial.
11. The vials were not amended with nutrients since it was intended for the microcosms to be most representative of field conditions.
12. The contaminant concentration in the groundwater was considerably higher than the concentration in the soil, and it was considered that this may have overloaded the microorganisms and thereby cause underestimation of the rate of biodegradation. Consequently, the groundwater was diluted 50/50 with distilled water because the concentration of contaminant was greater in the groundwater than in the soil. Thus, 15% soil and 85% water, by volume, was used. The actual contaminant concentration in the slurry of soil and water was determined by

$$C_1V_1\ (\text{soil}) + C_1V_1\ (\text{groundwater}) + C_1V_1\ (\text{distilled water}) = C_2V_2\ (\text{slurry})$$

13. Each vial was flushed with N_2 gas while the groundwater was added to maintain an anaerobic environment. They were then sealed with Teflon-lined butyl rubber septa and aluminum crimp caps. The N_2 gas flushing was done in the headspace of each vial, making sure not to flush the liquid, while ensuring N_2 gas entered the vial.
14. The negative controls were sterilized by autoclaving (3 times) at 121°C (About 30 min to 60 min each time) to ensure complete sterilization. However, following the sterilization, it was determined that the contaminants had volatilized from the groundwater during sterilization. The negative controls were subsequently spiked with a prepared solution of contaminants.

15. Sampling times were planned to be 0,5,8,10,15,25,30,35,40,45,50,60,70,80,90 (days) but were changed to follow the schedule shown in Table E-1.
16. Destructive sampling was used, in which each vial was sacrificed for a particular sampling event.
17. After each sampling event, all the remaining microcosms were inverted once to mix them and still allow the soil to settle in each vial before the next sampling event.
18. Concentration of contaminants were measured during each sampling event by extracting the supernatant from the vial and analysing it with purge and trap followed by gas chromatography with a flame ionization detector. 5 mL of diluted supernatant were injected into the sample holder for purge and trap. The vials, each consisting of 15 g soil and 25 mL groundwater, were sacrificed in triplicate on each sampling event. For the well 27 samples, 0.2 mL of supernatant (approximately 4850 μg/L TCA) was withdrawn, diluted in 25 mL deionized water in a volumetric flask and mixed (to make approximately 40 μg/L TCA). A 5 mL aliquot of the mixture was then injected into the purge and trap concentrator for analysis. For the well N samples, 0.8 mL of supernatant (approximately 1250 μg/L TCA) was withdrawn, diluted in 25 mL deionized water and mixed in a volumetric flask (to make approximately 40 μg/L TCA). A 5 mL aliquot of the mixture was then injected into the purge and trap concentrator for analysis. The reason for the dilution of the supernatant was to prevent overloading of the gas chromatograph column. The amount of supernatant withdrawn for dilution was varied depending on the concentration of TCA presumed to remain in the sample vials.
19. Mass of contaminant adsorbed to soil was taken as initial mass of contaminant minus the final mass of contaminant at a particular time in the negative controls containing soil.

20. To check the operation of the purge and trap and the GC at every sampling event, a blank and a calibration standard (usually at 30, 40, or 50 µg/L) was tested, starting at day 0 to check GC recovery. The blank and standards were tested every 10 days

The microcosm procedure had to be modified while the microcosm tests were on-going. The sampling schedule for the microcosm vials is shown in Table E-1. Due to equipment malfunction with the gas chromatograph, the microcosm sampling program was delayed for 4 weeks after the fourth sampling event. After the GC was repaired, on December 12, 2001, the negative controls were spiked with filter sterilized solutions of 1,1,1-TCA, 1,1-DCA, 1,3-DCB, 1,4-DCB, and 1,2-DCB to resemble the original concentrations present in the groundwater.

The negative controls were spiked before the December 12 sampling event. Filter sterilized chemical standards of TCA, DCA, 1,3-DCB, 1,4-DCB, and 1,2-DCB were injected into each negative control. Approximately 9700 µg/L of TCA and 1900 µg/L DCA was injected into each Well 27 negative control and approximately 2500 µg/L of TCA and 660 µg/L DCA was injected into each Well N negative control. The butyl rubber septa were wiped with ethanol before injection of the chemical standards to minimize the entrance of microorganisms into the microcosm vials during injection. Although a known concentration of standards were injected into each negative control vial, it was possible that the resulting concentration of each compound (TCA, DCA, or the DCBs) in the negative controls would be greater than that injected. The reason for the difference was the possible presence of some residual concentration of each compound in each vial before injection.

Quality control

As noted in the microcosm test procedure list, for quality control, a blank sample of deionized water was analyzed through the GC. If the chromatogram showed a smooth baseline with no contaminant peaks, the remaining tests could then proceed. During each sampling event, a known concentration solution prepared from standard stock was analysed through the GC to determine the percent recovery and thereby chart the reliability of the GC results for that sampling event. Figures E-1 and E-2 show the results for the quality control. The plots show that there was good agreement between the expected concentrations and the analysed concentrations. Percent recovery was between 80% to approximately 115%.

Table E-1: Microcosm Test Sampling Events

	20-Oct-00	23-Oct-00 24-Oct-00	25-Oct-00 26-Oct-00	28-Oct-00	12-Dec-00 13-Dec-00	18-Dec-00 19-Dec-00	29-Dec-00 30-Dec-00	08-Jan-01 09-Jan-01	18-Jan-01 19-Jan-01	28-Jan-01 29-Jan-01	06-Feb-01 07-Feb-01	08-Feb-01 09-Feb-01	20-Feb-01 21-Feb-01	27-Feb-01 28-Feb-01	10-Mar-01 11-Mar-01	20-Mar-01 21-Mar-01
Time (days)	0	3 to 4	5 to 6	8	53 to 54	59 to 60	70 to 71	80 to 81	90 to 91	100 to 101	110 to 111	112 to 113	124 to 125	131 to 132	142 to 143	152 to 153
Regular sacrifice (20°C)	6	6	6	6	6	6	6	6	6	6	6	0	6	6	6	6
Regular sacrifice (10°C)	6	6	6	6	6	6	6	6	6	6	0	6	6	6	6	6
Negative controls (20°C)	2	2	2	2	2	0	2	2	0	2	2	0	2	2	2	0
Negative controls (10°C)	2	2	2	2	2	0	2	2	0	2	0	2	2	2	2	0
Quality control	1 blank 3x3 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal	1 blank 1 cal

Figure E-1: Quality Control For Each Sampling Event (Recovery of 1,1,1-TCA Standard)

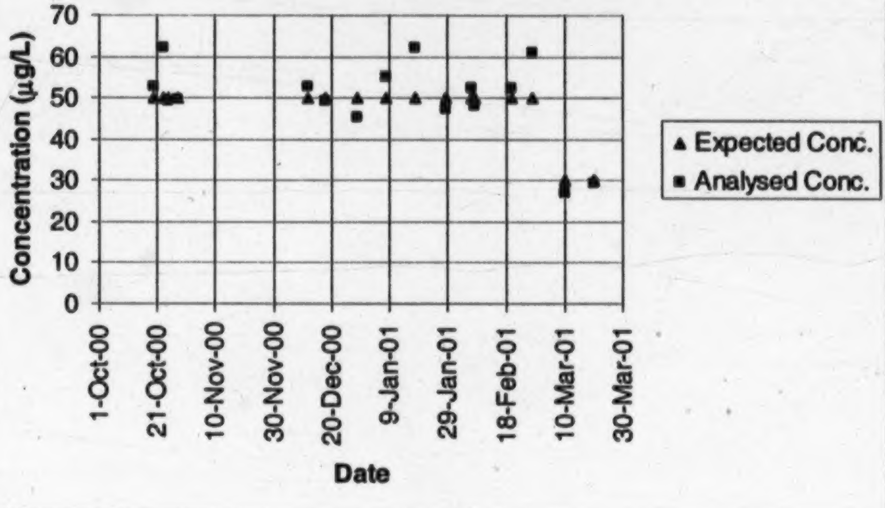


Figure E-2: Quality Control For Each Sampling Event (Recovery of 1,1,1-TCA Standard)